University of Albert a

THE SYNTHESIS AND DERIVATIZATION OF AN α,α-DIBROMOYNONE AND RELATED METHODOLOGY

by

TRENT JOSEPH RANKIN ©

A thesis subitted to the Faculty of Graduate Studies and research in partial fulfillment of the requirement for the degree of Master of science

Department of Chemistry, U of Alberta

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27 Sept 2002

Date of Thesis Approval

Abstract

The synthesis of a series of highly functionalized vinyl triflates has been accomplished by the derivatization of an α,α-dibromoynone. The methodology used in the synthesis is described herein. Palladium catalyzed cross-coupling techniques were employed as the primary methods for the construction of these compounds. The analysis of all compounds is detailed, including ^1H NMR, ^{13}C NMR, and IR spectroscopy, as well as high resolution mass spectrometry and in certain cases melting points and elemental analysis.

Acknowledgements

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List of Symbols, Nomenclature and Abbeviations

Å	angstrom(s)
Ac	acetate
APT	attached proton test
aq	aqueous
Bu	butyl
C-C	carbon-carbon
d	doublet
dd	doublet of doublets
deg	degree(s)
DMF	dimethylformamide
EDG	electron donating group
Et	ethyl
equiv	equivalent
EWG	electron withdrawing group
g	gram(s)
h	hour(s)
HMDS	hexamethyldisilazane

HMPA	hexamethylphosphorictriamide
Hz	hertz
IR	infrared
m	multiplet
Me	methyl
mg	milligram(s)
MHz	megahertz
min	minute(s)
mL	milliliter(s)
mmol	milimole(s)
mol	mole
Mp	melting point
MS	mass spectrometry
m/z	mass-to-charge ratio
nm	nanometer
NMR	nuclear magnetic resonance
ORTEP	oak ridge thermal ellipsoid plot
Ph	phenyl

Pr	propyl
rt	room temperature
s	singlet
t	triplet
t	tertiary
TES	triethylsilyl
Tf	triflate, trifluoromethanesulfonyl
THF	tetrahydrofuran
TIPS	triisopropylsilyl
TLC	thin layer chromatography
TMS	trimethylsilyl
UV	ultraviolet
Vis	visible

I INTRODUCTION

1 Palladium Catalyzed C-C Bond Formation

The development of metal mediated cross coupling reactions has led to a broad variety of new methodology.[1] In particular, palladium catalysis has been found to be most instrumental in the creation of carbon-carbon bonds. The ease of catalyzed reactions and their tolerance to functional groups has led to the extensive applicability of palladium in this area. All types of C-C bonds have been constructed through this methodology, and recent literature shows that many groups are involved with the development of new palladium catalyzed methodology.

Of the variety of palladium catalyzed C-C bond forming reactions, few involve sp^3 hybridized carbon centers.[2] This is currently a challenge in organic synthesis where work is in progress.[3] The majority of cross-coupling reactions involve sp or sp^2 carbon centers for reaction, leading to the formation of conjugated bonds. Palladium catalyzed methodology maintains the stereochemistry of conjugated bonds to a large extent. These resultant structures are also important to many types of chemistry, such as polymers or materials.[4]

Although palladium catalysts have been developed to optimize particular reactions, there are only a few that are used extensively. The use of $Pd(PPh_3)_4$ is common, although $PdCl_2(PPh_3)_2$ and $Pd(OAc)_2/PPh_3$ are less air sensitive and can therefore be easier to employ. Unusual ligands that coordinate to palladium can lead to enhanced reactivity[5] and may be required for the synthesis of stereogenic centers. Even though the synthesis of these specialized palladium complexes can be tedious and expensive, they can have exceptional properties, justifying their synthesis. For example, catalysts have been developed with the ability to react with aryl chlorides[5], which are normally unreactive to cross-coupling, but are readily available. These catalytic properties may create demand for a greater variety of commercially available catalysts. As this thesis focuses on the various types of palladium catalyzed cross-coupling reactions, catalyst development will not be discussed but has been reviewed elsewhere in literature.[1,6]

Although there are several catalysts that are most often employed in cross-coupling reactions, optimized conditions may need to be established for specific transformations. Solvent, temperature, base, and catalyst ligands all may affect the yield or the reaction progression. These factors play different roles in the different types of cross-coupling reactions as well. It may appear that reagents are used without methodical format, but there are general rules that can be applied to each cross-coupling reaction. These will be discussed as each type of methodology is evaluated.

The mechanistic sequence for palladium catalyzed C-C bond formation, although debated, is believed to proceed first by oxidative addition of an electrophile to the palladium species. A variety of organic electrophiles, such as vinyl or aryl halides and triflates, are able to react by cross-coupling with palladium catalysts. The order of reactivity is generally I > OTf > Br > Cl.[7] The oxidative addition of palladium into the carbon-halide or carbon-triflate bond can often be the rate determining step in the catalytic cycle. This means that the choice of the electrophile may be important to the success of a reaction. To understand the palladium catalyzed cross-coupling process, a general mechanistic sequence of the cross-coupling reaction is shown below (Figure 1).[7]

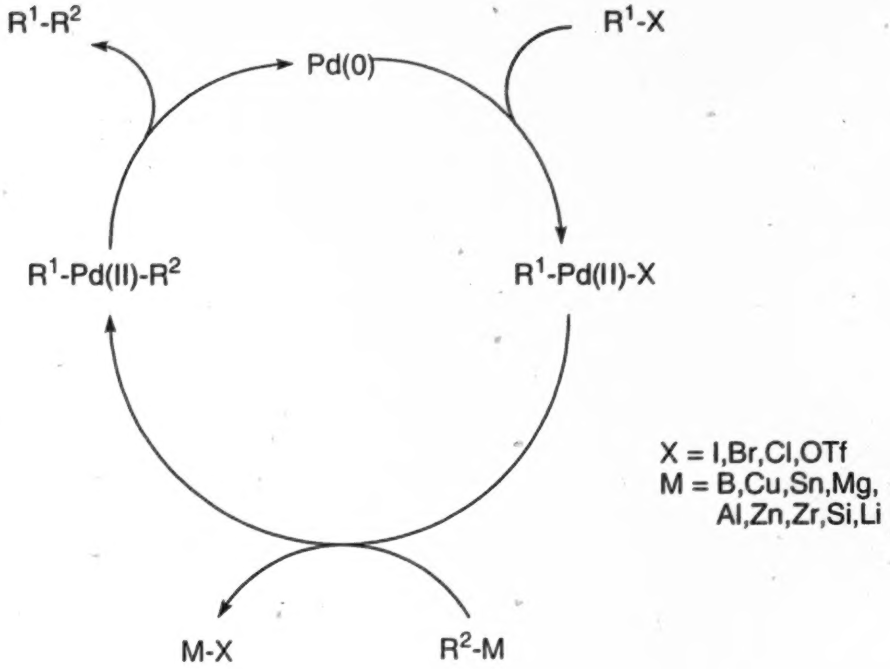

R^1-R^2
Pd(0)
R^1-X
R^1-Pd(II)-R^2
R^1-Pd(II)-X
X = I,Br,Cl,OTf
M = B,Cu,Sn,Mg,
Al,Zn,Zr,Si,Li
M-X
R^2-M

Figure 1. A General Catalytic Cycle for Palladium Catalyzed Cross-Coupling Reactions

The next step in the mechanism is the transmetalation of an organometallic species (R^2-M) to the catalyst. The catalyst, now with the two differing organic ligands, then effects C-C bond formation via reductive elimination.[8] Within this mechanistic sequence there may be additional steps such as ligand loss or substitution at the palladium center. It is cited in literature that anionic intermediates may be involved in some cases, dependent upon the halide or alkoxide ligands present.[8]

Palladium remains in a Pd(II) oxidation state for most of the catalytic cycle, although it is initially in a Pd(0) state and is reduced back to Pd(0) again at the end of the mechanistic sequence. In the case of a Pd(II) precatalyst, such as $PdCl_2(PPh_3)_2$, the requisite Pd(0) species can be generated via *in situ* reduction. For example, oxidative homocoupling of reagents or reaction with phosphine ligands are two possibilities.[9]

In order for the experimentalist to assemble the structure that they intend, varying methodologies must be used. Preparation of starting materials and their tolerance to reaction conditions must be evaluated. The following is a synopsis of common methods for palladium catalyzed C-C bond formation and some of their advantages and disadvantages. Methods used throughout this thesis are the major focus of discussion, while other methods will be described in lesser detail. It is intended that the following will provide only a general overview of common palladium cross-coupling reactions.

1.1 sp – sp^2 Carbon Coupling

The ability of a terminal alkyne to be coupled to vinyl or aryl halides and triflates in the presence of a palladium catalyst, a base, and catalytic CuI is termed the

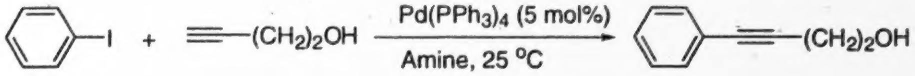
Sonogashira reaction (equation 1).[10] The reaction, reported by Hagihara and Sonogashira,[11] is the preferred route when an arylyne or enyne moiety need be constructed in a molecule.

$$\mathrm{R{-}{\equiv}{-}H} \quad + \quad \mathrm{X{-}R'} \quad \xrightarrow[\text{amine}]{\text{[Pd], CuI}} \quad \mathrm{R{-}{\equiv}{-}R'} \qquad \textbf{(1)}$$

R = aryl, alkyl, SiR_3, alkynyl, alkenyl
R' = aryl, alkenyl
X = I, Br, OTf

The addition of a Cu(I) halide to the reaction results in a marked rate acceleration.[11] This is likely due to the formation of a copper acetylide species *in situ*. It is well known that copper acetylides undergo cross coupling reactions with vinyl/aryl halides, a sequence known as the Stephens-Castro reaction.[12] The base used in the reaction (usually an amine) can serve to create a nucleophilic acetylide prior to the copper acetylide species and, in some cases, to remove the HX which is formed during the reaction.[13] It is possible that the base could act as a ligand for the palladium species as well. There have been reports that certain bases increase the reaction rate, but this must often be determined experimentally for a given situation (Table 1).[14] The information shown in Table 1 is remarkable for several reasons, most notably that there is no copper present, and that the base facilitates the reaction. This data is likely not consistent with all reactions, but illustrates the importance of testing reagents. The bulkiness of a base may be detrimental, as *i*-Pr_2NH was not useful but *n*-$BuNH_2$ was successful. This is despite the fact that they do not differ greatly in basicity.

Table 1. Effect of Base on the Sonogashira Reaction

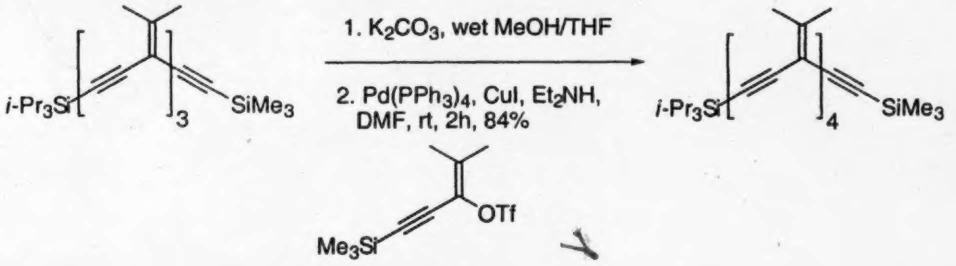


Entry	Amine	Time (h)	Isolated Yield (%)
1	Et_3N	22	0
2	*i*-Pr_2NH	26	2
3	Et_2NH	24	0
4	*n*-$BuNH_2$	25	93
5	piperidine	6	96
6	pyrrolidine	2.5	91

It is common to use an amine as both base and solvent, although this depends on the solubility of the reagents. If preferred, only a few equivalents of base are required. Solvent has not been shown to have a predetermined effect in the Sonogashira reaction and must therefore be optimized through individual experimentation. Common solvents employed are DMF and THF.

There are several other key points to consider in order to successfully accomplish the Sonogashira reaction. Care must be taken to eliminate oxygen from the reaction, as this will decrease oxidative homocoupling of the acetylene and prevent degradation of the catalyst (if air sensitive). Vigorous bubbling of an inert gas through the solvent for approximately 30 min is usually sufficient. The reaction is also known to be sensitive to the electronic nature of the aryl halide or triflate cross-coupling partner. An electron withdrawing group *para* or *ortho* to the halide or triflate has been shown to accelerate the reaction, whereas electron donating groups in these positions dramatically reduce reaction rates.[15] Heat is typically used to accelerate sluggish reactions, such as those using vinyl or aryl bromides. Recent catalytic systems have shown that room temperature cross-coupling reactions of arylbromides are possible.[16] These systems often employ reagents not common to most laboratories however, such as unusual phosphine ligands or ionic liquids for solvent.

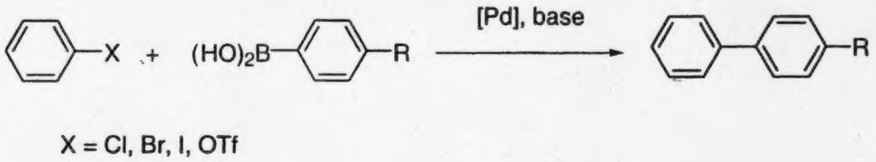
The cross-coupling products from the Sonogashira and related reactions include enyne structures, common to materials such as liquid crystals or oligomers (equation 2).[17] Typical Sonogashira conditions are mild and easily tolerated by most substrates. The advantages listed above illustrate the versatility of this method, and rerports that exploit this methodology are common.


i-Pr3Si
3
SiMe3
1. K2CO3, wet MeOH/THF
2. Pd(PPh3)4, CuI, Et2NH, DMF, rt, 2h, 84%
OTf
Me3Si
i-Pr3Si
4
SiMe3

(2)

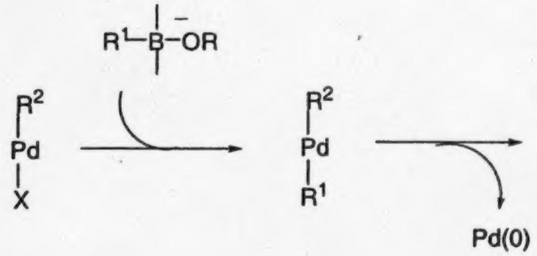
1.2 Bond Formation Using Organoboron Compounds

The ability of boron to transfer aryl or vinyl functionality to palladium has allowed for a wealth of synthetic work.[18] A variety of organoboron compounds can be applied to this reaction, such as boronic acids or esters, or even trialkyl boron derivatives. The organoboron substrate can be coupled with a triflate or halide using a base and palladium catalyst, effecting C-C bond formation, a process referred to as the Suzuki reaction (equation 3), in honor of Akira Suzuki.[19]


X
+
(HO)2B
R
[Pd], base
R
X = Cl, Br, I, OTf

(3)

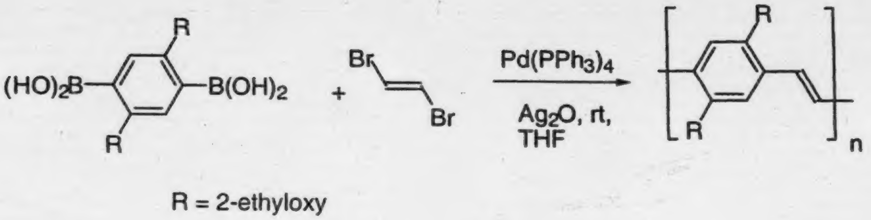
A strong base is employed in most cases (typically an alkoxide), although base sensitive compounds can sometimes be utilized in this reaction without detriment to the sensitive functionality.[20] There are differing opinions as to why the base is required, with the general consensus being that the formation of an ate complex involves boron, just prior to transmetalation (equation 4).[7] It is also proposed that the base may coordinate to palladium during the reaction, forming an electron rich palladium species.[21] Even so, there are literature reports of successful reactions that do not require base, or that employ mild bases suspended in organic solvents.[22]

 (4)

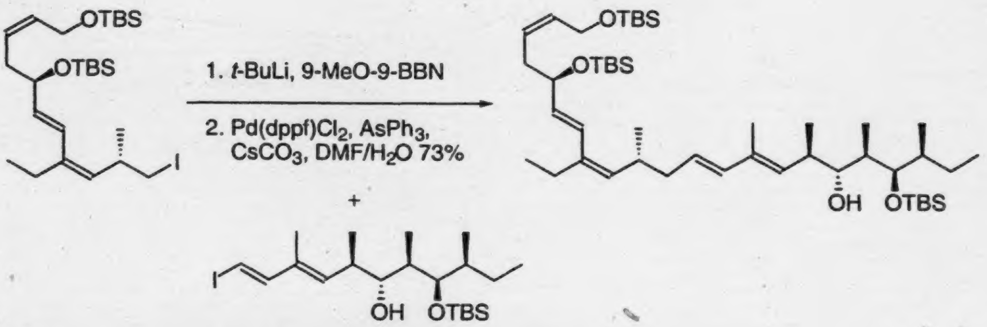
As with most palladium catalyzed reactions, the Suzuki protocol requires a strict absence of oxygen to prevent homocoupling of the organometallic species or degradation of the catalyst. The solvent can be varied to meet the solubility requirements of the reaction. Organoboron compounds are often stable to air and water, and few are thermally labile. As well as these attributes, there are many well known routes for the incorporation of boron into organic compounds. The hydroboration reaction has been well studied, and can be used to yield products of anti-Markovnikov addition upon reaction with alkynes.[7] These types of reactions are regioselective, and often stereoselective for the generation of alkenyl boron compounds. Also, borates are good electrophiles for nucleophilic attack, yielding boronic acids upon work up.

The drawback to the use of organoboron compounds, in particular boronic acids, is that they can be difficult to purify. There have been recent developments in the purification of boronic acids, although only on small scale.[23] For example, the use of solid support allows for substrates containing a boronic acid to be cleaved after several synthetic steps, yielding very pure products.[23]

Synthetically, the Suzuki reaction has become important to many types of chemistry. For example, the Suzuki reaction has been used successfully to generate polymers (equation 5).[4] Furthermore, the reaction has become important to the synthesis of natural products, such as the intermediate step in the recent total synthesis of (-)-Callystatin A (equation 6).[24] This step features an interesting Suzuki sp^3-sp^2 coupling by way of a preformed ate complex. This example illustrates the potential of this methodology to afford synthetic transformations that would otherwise be difficult to achieve.


(HO)$_2$B
B(OH)$_2$
R
R
+
Br
Br
Pd(PPh$_3$)$_4$
Ag$_2$O, rt,
THF
R
R
n
R = 2-ethyloxy

(5)


OTBS
OTBS
I
1. t-BuLi, 9-MeO-9-BBN
2. Pd(dppf)Cl$_2$, AsPh$_3$,
CsCO$_3$, DMF/H$_2$O 73%
+
I
OH
OTBS
OTBS
OTBS
OH
OTBS

(6)

1.3 Bond Formation via Stannanes

Another widely used organometallic reagent in cross-coupling reactions is the organostannane. The use of stannanes in palladium catalyzed cross-coupling is referred to as the Stille reaction, as the late John K. Stille was influential in this field of chemistry (equation 7).[25] This reaction can be accomplished because tin is able to specifically transfer one of its organic groups to palladium. This allows for the subsequent cross-coupling with all electrophilic partners listed beforehand. After the lone non-alkyl group has been transferred to palladium, there is a significant rate deterioration for the transmetalation of the remaining groups from the trialkyltin halide. This is because the alkyl groups left on tin are poor cross-coupling partners.

$$R_3Sn{-}R' \quad + \quad X{-}R'' \xrightarrow{[Pd]} R{-}R'' \quad + \quad R_3SnX \qquad \textbf{(7)}$$

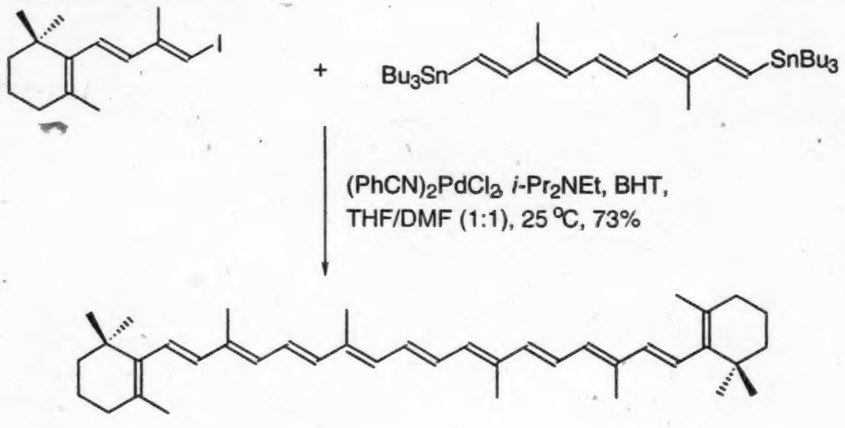
$$X = Cl, Br, I, OTf$$

The Stille reaction is one of the most fundamentally simple cross-coupling reactions to accomplish. The only requirements are the organotin species, an electrophile, and a palladium catalyst. A few generalities for this reaction can be distilled from literature. In some cases oxygen does not have to be rigorously excluded from the reaction, depending on the nature of the catalyst. Solvent can have a great influence on the reaction outcome, and highly polar organic solvents are a typical choice.[25] Heat can accelerate the reaction, and most tin species are thermally stable. In addition, it is noteworthy that the addition of LiCl has been shown to aid in the cross-coupling with triflates.[26] This may be due to the addition of the chloride ion to the catalyst at some point.[27]

Organotin compounds are often easier to purify than other organometallic counterparts, and many different routes for their synthesis have been developed. Tin hydrides can react by addition to a triple bond, although the reaction is usually not stereospecific, and thus lead to mixtures of products. Recent methodology employing carbostannnylation via Ni or Pd catalysis generates enyne and diene structures in high yield containing the trialkyltin moiety.[28] It is also quite common to use electrophiles such as trimethyl or tributyl tin chloride to trap nucleophiles, yielding products suitable for subsequent cross-coupling reactions. It is due to this abundance of methodology that the stannane functionality can be introduced late in a stepwise sequence.

There are, however, drawbacks to the Stille reaction; a major one is that tin(IV) compounds are not environmentally friendly and are often quite toxic. Care must be taken in the handling of starting materials and disposal of waste. Tin residues can also be difficult to remove from the products. There are a few methods to remove tin, such as using a fluoride source, but not all compounds will be stable to these reagents.[29]

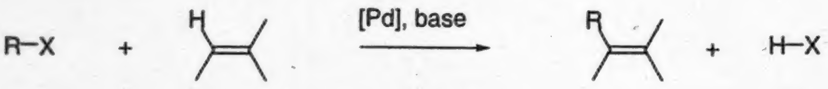
The Stille reaction has been widely used throughout organic chemistry, and examples are too numerous to cite. Shown below is one recent example where this reaction is used to generate a complex natural product (equation 8),[30] a carotenoid, by way of a two-fold symmetrical coupling. The reaction takes place with no loss of stereochemistry.


I
+
Bu3Sn
SnBu3
(PhCN)2PdCl2, i-Pr2NEt, BHT,
THF/DMF (1:1), 25 °C, 73%

(8)

1.4 Bond Formation Involving a Vinylic Hydrogen

The palladium catalyzed arylation or vinylation of olefins is known as the Heck reaction, after F.R. Heck (equation 9).[31] This reaction has been extensively developed, including asymmetric variants,[32] which create new stereogenic centers of absolute configuration.


R–X
+
H
[Pd], base
R
+
H–X

(9)

X = Cl, Br, I, OTf

The Heck reaction requires base, a vinylic hydrogen, an electrophile, and a catalyst. The Heck reaction follows a different catalytic cycle than outlined in

Figure 1, in that there is no transmetalation step. The organopalladium species undergoes carbopalladation by addition to an olefinic bond, followed by β-hydride elimination (Figure 2). An interesting point regarding the Heck reaction is that the base serves to scavenge the proton on the palladium species after the β-hydride elimination step, which releases the product.[32] Some commonly used bases include trialkyl amines and weak alkoxides.

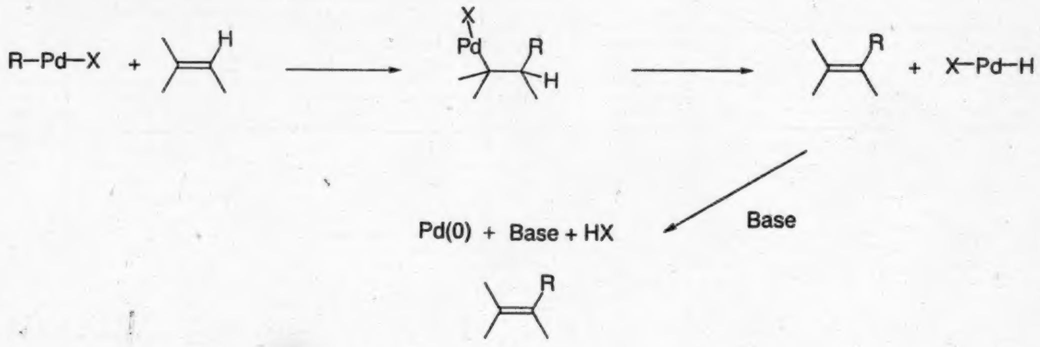
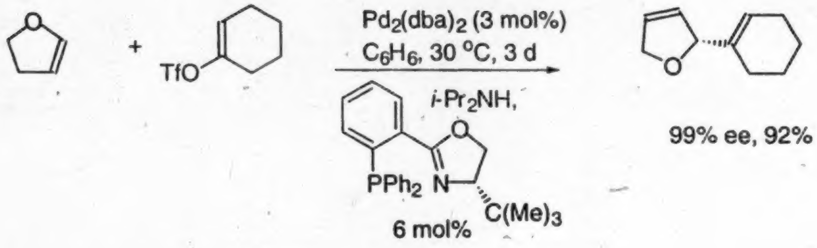


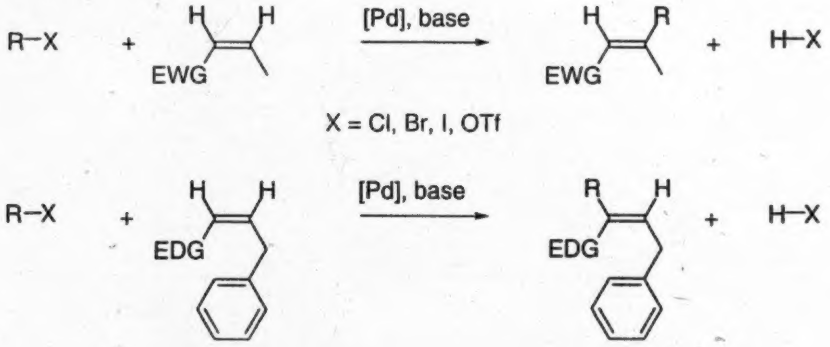
Figure 2. Mechanism of the Heck Reaction

The Heck reaction does not require an inert atmosphere, although excluding oxygen does prevent the formation of phosphine oxides. The catalyst used can be specific to desired reactions, especially when generating stereocenters. The reaction below employs a chiral ligand to promote an enantioselective Heck reaction (equation 10).[33]


TfO
Pd$_2$(dba)$_2$ (3 mol%)
C$_6$H$_6$, 30 °C, 3 d
i-Pr$_2$NH,
PPh$_2$
C(Me)$_3$
6 mol%
99% ee, 92%

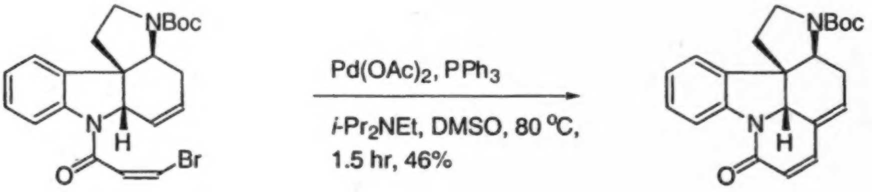
(10)

An advantage to the Heck reaction is its high chemoselectivity. Alkenes bearing two vinyl hydrogens can be used, and there are a few trends that can be predicted for the regiochemical outcome when this is the case (Scheme 1). If an electron withdrawing group is present on the olefin, the organic group is often transferred to the distal carbon of the olefin. In the case of an electron donating substituent or an unsymmetrical olefin, bond formation usually occurs at the less sterically crowded carbon.[34]


R–X
EWG
[Pd], base
H–X
X = Cl, Br, I, OTf
EDG

Scheme 1. Regiochemistry of the Heck Reaction

The Heck reaction is a very useful cross-coupling method in organic synthesis. There is no requirement for an organometallic component, only an olefin. With less functionality required, this sequence is easy to implement. The Heck reaction also has less waste associated with it, with no metal by-products. The example shown below illustrates the recent use of the Heck reaction to effect an intramolecular ring closure toward a substructure of strychnine (equation 11).[35]

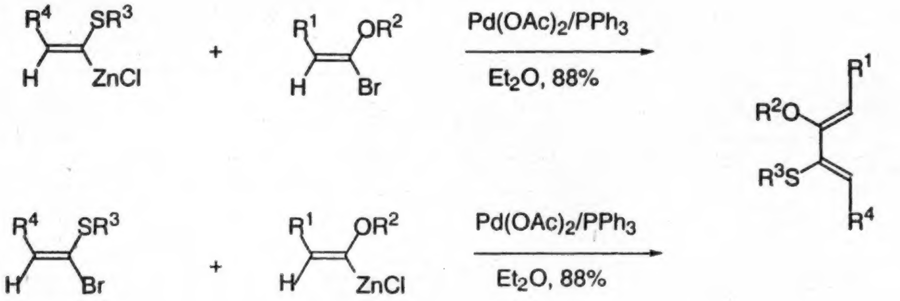


(11)

1.5 Bond Formation Employing Zn, Al, and Zr Reagents

The ability of an organozinc, aluminum or zirconium species to cross-couple with organic electrophiles in the presence of a palladium catalyst is known as the Negishi reaction, after Ei-ichi Negishi.[36] Organozinc chlorides can be more reactive than the corresponding stannanes, on occasion enabling reactions that otherwise failed under Stille conditions. The Negishi reaction is of synthetic utility when the organometallic component can be synthesized, but the lack of varied methodology for the synthesis of these organometallic derivatives leaves the method less widely used.

Organozinc and organozirconium compounds are typically synthesized from the corresponding Grignard or organolithium species via reaction with the metal halide. An exception to this trend is aluminum. Aluminum reagents can react via hydrometallation and carbometallation, yielding products useful for cross-coupling reactions. A recent example of the Negishi coupling is shown below (equation 12), and illustrates the tolerance of organozinc compounds towards various functional groups.[37]

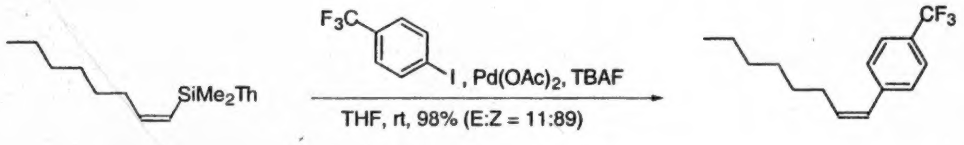


(12)

1.6 Bond Formation via Si Reagents

Recent work by Tamejiro Hiyama has shown that organosilicon compounds can undergo cross-coupling reactions. A recent example illustrates that, although there is some loss of stereochemistry, this can be a powerful synthetic method (equation 13).[38] The mechanistic sequence is believed to involve a pentacoordinate silicon species that is then transmetallated to palladium. The use of a fluoride source by Hiyama creates an anionic silicon species, polarizing the normally non-polar carbon silicon bond.[39] Hydroxide ions are also able to generate this same effect.

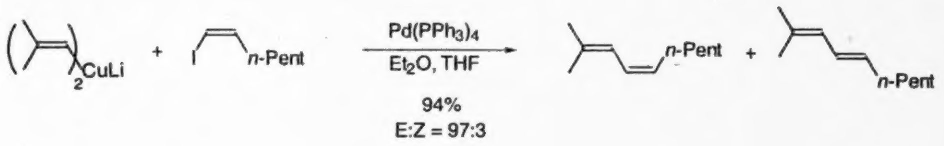
An advantage of this type of cross-coupling reaction, often called the Hiyama reaction, is that it allows for silicon protected alkynes to undergo cross-coupling without prior deprotection. Silicon waste products are also not as harmful as any of the metals previously mentioned. A recent review covers this area of chemistry quite well.[40]



(13)

1.7 Bond Formation Via Cu Reagents

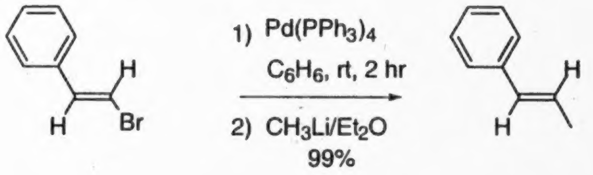
The Normant reaction is when an organocuprate reagent undergoes cross-coupling via palladium catalysis with an electrophile (equation 14).[41] Organocuprates can be synthesized through carbometallation reactions with alkynes, leading to stereoisomeric products. These products can then be utilized in cross-coupling reactions. The mildness of the reagents and the affordability of the starting materials make this a well utilized reaction. The synthesis of the cuprate reagent can, however, be difficult, making the reaction inefficient. There is also an accompanying loss of stereochemistry.



(14)

1.8 Bond Formation via Mg and Li Reagents

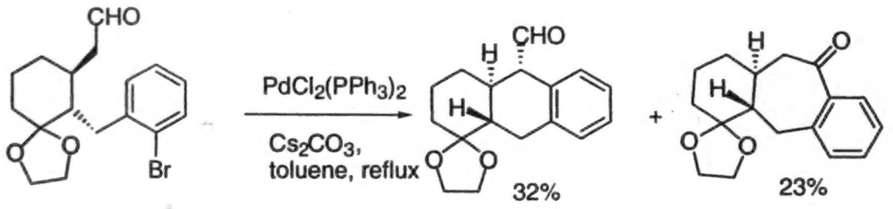
The ability of organolithium or Grignard reagents to participate in palladium catalyzed cross-coupling reactions is commonly called the Murahashi reaction, after Shun-Ichi Murahashi (equation 15).[42] The drawback to using such strong nucleophiles is that halogen-metal exchange can occur with the halide cross-coupling partner. To successfully complete this type of cross-coupling reaction, a stoichiometric amount of the reagent is often used with slow addition to the other coupling partner. Other organometallic reagents avoid this necessity, rendering them more widely used.



(15)

1.9 Palladium Catalyzed Reactions not involving Organometallic Reagents

The ability of a non-organometallic nucleophile to react directly in palladium catalyzed cross-coupling reactions has been the subject of much recent research.[43] This type of reaction allows for the incorporation of many types of functional groups. The reaction works well with arylated halides, giving a convenient route into intramolecular reactions (equation 16).[44] An advantage to such reactions is that they avoid the use of the organometallic reagent, resulting in less waste and simplified reactions.

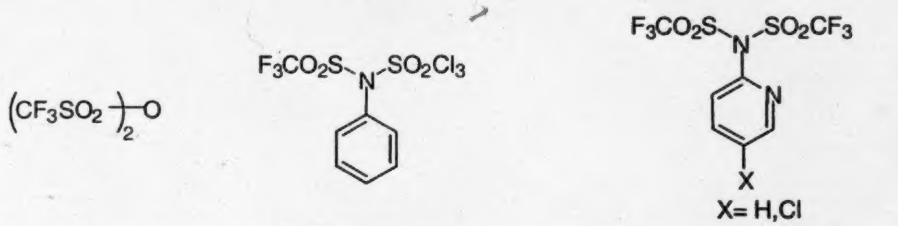


(16)

2 Fluorinated Sulfonates

Fluorinated sulfonates stand out as perhaps the most versatile of the electrophilic partners for palladium catalyzed cross-coupling reactions. They can be generated from a host of starting materials, such as ketones, alcohols, and lactones. The advantage of fluorinated sulfonates is that they can be introduced at an advanced stage in the synthesis, often from a protected precursor. This section will try to break down some of the various methods for fluorinated sulfonate synthesis on the basis of their utility.

In general, these reagents can be classified into two groups: trifluoromethanesulfonates (triflates), and nonafluorobutanesulfonates (nonaflates). There are other less utilized fluorinated sulfonates, but due to convenience and applicability, only the triflate seems common. The triflate group is commonly generated through trapping of an enolate or alkoxide. Some of the various electrophiles for triflation are shown below (Figure 3).[45]

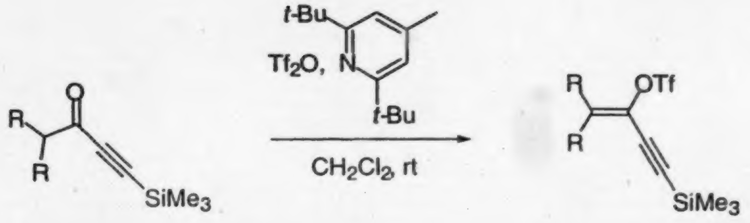


Triflic Anhydride   *N*-Phenyltriflimide   *N*-Pyridyltriflimide

Figure 3: Electrophiles used for triflation

Triflic anhydride is very commonly used in the synthesis of aryl or vinyl triflates. Less reactive reagents such as *N*-phenyltriflimide or *N*-pyridyltriflimides are also commonly employed. There are other less common triflating agents, such as trifluoromethanesulfonylimidazole or trifluoromethanesulfonylchloride. The synthesis of nonaflates requires either of two reagents: nonafluorobutanesulfonylfluoride or the corresponding anhydride. In many cases, it has been shown that nonafluorobutanesulfonylfluoride results in a cleaner reaction.[46] As the triflate is a more widely utilized functional group in cross-coupling reactions, priority will be given to methods for its synthesis. There are many methods throughout literature for the synthesis of so-called kinetic or thermodynamic enolates. Hindered bases at low temperatures are used for the formation of kinetic enolates, while equilibrating conditions are employed for the synthesis of thermodynamic enolates.[47] Once the desired enolate has been formed, it is simply a matter of trapping with the triflate source. Optimized reaction conditions are varied, and the appropriate triflate source will need to be determined experimentally. To follow is a synopsis of common methodology for the formation of triflates from enolates.

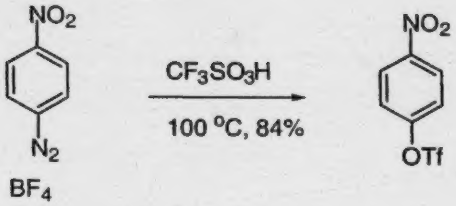
Difficult triflates to form, such as those derived from lactones, have been synthesized via deprotonation with LiHMDS in the presence of HMPA, followed by trapping with *N*-phenyltriflimide.[48] Triflate formation is commonly effected by adding a ketone precursor to a solution containing a hindered base such as 2,6-di-*t*-butyl-4-methylpyridine and triflic anhydride (equation 17).[49] It is known that bases may react with triflic anhydride, and the use of a hindered base prevents this undesired side reaction.



(17)

It has been shown that α,β-unsaturated ketones can be used to generate enolates via Li/NH_3 reduction or by dialkylcuprate additions. The resulting enolate can then be easily trapped as a vinyl triflate.[45] Another method for triflate formation is *in situ* trapping of an enolate formed from a pre-existing vinyl species. For example, silyl enol ethers can be transformed into the analogous triflate by removal of the silyl group with methyllithium, followed by trapping with *N*-phenyltriflimide.[50]

Aryl triflates can be synthesized through the use of either an amine or alkoxide base for deprotonation, followed by trapping with a triflate source. Due to the stability of aryl alkoxides, there are fewer problems associated with the formation of these types of fluorinated sulfonates. Another route to aryl triflates uses aryldiazonium salts. These compounds were shown by Suzuki to decompose thermally or photochemically in triflic acid, yielding substituted aryl triflates (equation 18).[51]



(18)

Although fluorinated sulfonates are known to be good leaving groups, it is their ability to undergo cross-coupling reactions that is of interest to the work outlined in this thesis. These triflate compounds react under all cross-coupling conditions mentioned in Section 1.

3 Cross-Conjugated Compounds

The intense development of materials research has brought organic molecules to the forefront of areas previously dependent on inorganic compounds. The industry involved in electronics[52] and optics[53] has been studying organic compounds as potential media for applications in these fields. Much research to date has been focused on the use of conjugated molecules for these areas of chemistry, as their synthesis and properties are well known. Less understood in terms of their possible materials behavior are cross-conjugated compounds. Cross-conjugated compounds are defined as those that have at the least three unsaturated bonds, two being at any moment conjugated to each other but not to the third. An examination of π-bonding in a small cross-conjugated molecule, 3-

methylene-1,3-pentadiene, shows that according to the molecular orbital theory description there is net bonding throughout the π structure and π-communication is present throughout, albeit limited.[54]

Experimental results from UV-Vis spectroscopic studies suggest that the π-electron communication is present throughout the cross-conjugated framework of certain compounds.[17] Furthermore, changes in donor-acceptor substitution patterns around these cross-conjugated structures been shown to alter their electronic properties.[55] An example of a cross-conjugated molecule is shown below, the extended radialene reported by Diederich and coworkers (Figure 4).[56]

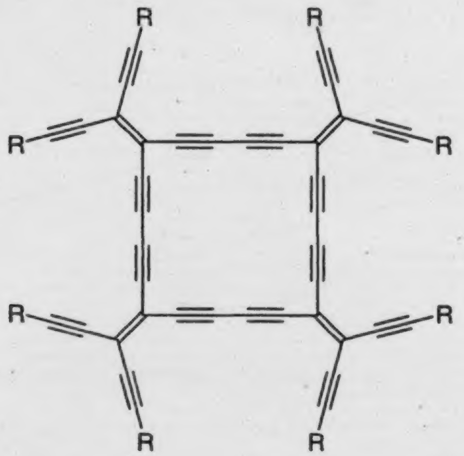


Figure 4 : Extended Radialene Reported by Diederich *et al.*

One interesting attribute of cross-conjugated materials is that these compounds may be transparent to light in the visible region of the spectrum. Linearly conjugated materials are often light absorbing in this range, which can limit their optical application at these wavelengths. The synthetic tools for the construction of cross-conjugated compounds are not yet as well developed as for other areas of organic chemistry. As a result there is wide potential for the study of cross-conjugated compounds.

4. Thesis Outline

The synthesis and properties of cross-conjugated oligomers has been of interest to materials chemistry in recent years.[17] The ability to generate these oligomers with defined length and purity has allowed for the systematic study of their properties. Two particular research areas employing cross-conjugated frameworks are functionalized macrocycles[57] and expanded radialenes (Figure 5).[58] These interesting structures can be constructed using a common building block, the vinyl triflate shown in Figure 6.

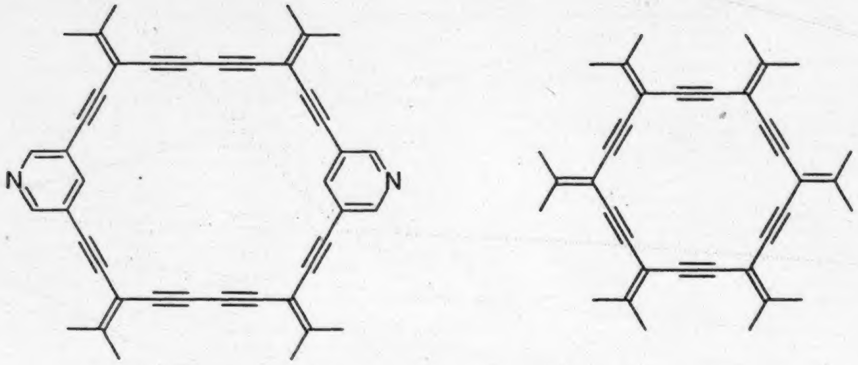


Figure 5. Macrocyclic Cross-Conjugated Compounds

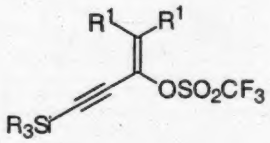
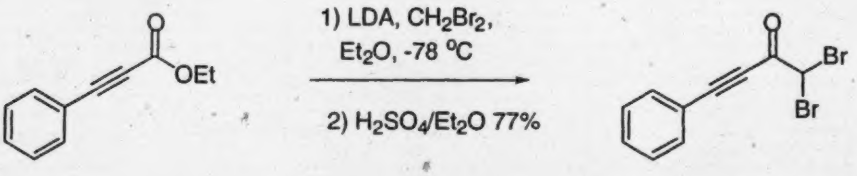


Figure 6. Building Block for Macrocycles and Oligomers

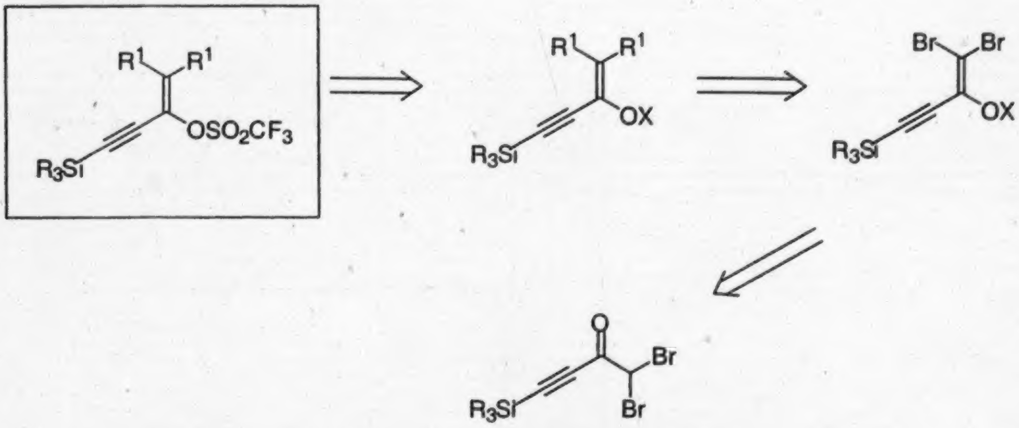
To date, the macrocyclic compounds (Figure 5) have been synthesized using simple alkyl or phenyl substituted analogues (e.g. R^1= Me, Ph) of this buiding block. One problem that has been encountered in the synthesis and study of many of these macromolecules is their limited solubility. The length of the oligomers and the rigidity of the macrocycles make for decreased solubility in common organic solvents. The problem of solubility can be alleviated by varying the pendant substituents (R^1) on the building block (see figure 6). The development of an easily adaptable synthesis for this structural component could also allow for the incorporation of interesting functional groups, such as electron withdrawing and donating moieties.

The research described herein outlines the synthesis of a silyl protected α,α-dibromoketone and its subsequent derivatization. It was anticipated that a range of desired vinyl triflate building blocks could be accessed starting with the synthesis reported by Barluenga and coworkers for a phenylated compound (equation 19).[59]



(19)

It was anticipated that once analogous dibromide compounds were synthesized, the structure could be converted into any number of dibromo-enyne structures (Scheme 2). Using palladium catalyzed methodology, different pendant substituents could then be incorporated. The ketone, protected for the transformation, could be regenerated and subsequently transformed into a vinyl triflate. This sequence would then be a viable route to the desired building blocks.

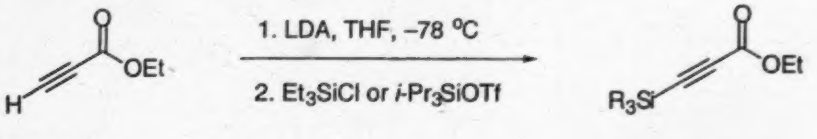

R1
R1
OSO2CF3
R3Si
OX
Br
Br
O

Scheme 2. Retrosynthesis of Vinyl Triflate Building Block

II RESULTS AND DISCUSSION

1 Formation of α,α-Dibromoketones

Using ethyl propiolate, a commercially available compound, the alkynyl moiety was protected with a silyl group. A commonly used protecting group is the triethylsilyl group (TES), for which Et_3SiCl was readily available. Literature methodology was employed, initially using *n*-BuLi in Et_2O at –78 °C for deprotonation, followed by trapping of the acetylide with Et_3SiCl.[60] However, this method resulted in a low yield of 44% and required distillation to purify the product. We predicted that a strong sterically hindered base such as LDA would decrease by-product formation. Also, TLC analysis indicated that, by changing the solvent to THF, the reaction progressed more cleanly. As a result of these alterations, the yield of compound **1** was increased to 94% (eq 20). Similarly, for the *i*-Pr_3Si protected compound **2**, a 94% yield was achieved. It is notable that the only purification required for **1** and **2**, is simple filtration of the impure oil through a small plug of silica gel with hexanes.

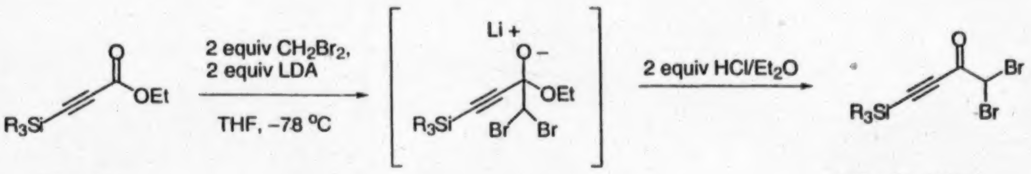


(20)

1 R = Et 94%
2 R = *i*-Pr 94%

Using ester **1**, the dibromomethylene functionality was incorporated by employing the Barluenga protocol (Scheme 3).[59] Following literature methodology, a mixture of ester **1** and dibromomethane in THF at –78 °C was treated with 2 equiv of LDA, affording *in situ* formation of the dibromomethyllithium species that then attacks the ester. The rationale for using two equivalents of base is that some of the dibromomethyllithium would likely react with dibromomethane. After 20 min, the mixture was quenched with conc. aq. HCl at –78 °C. This reaction sequence resulted in low yields of **3** (20-51%) and large quantities of dark tarry material.

Modified reaction conditions included a change in solvent to Et_2O. This resulted in a cleaner reaction, but after workup the tarry material remained and yields were not increased (55%). We suspected that acid catalyzed aldol chemistry may have been causing some of the observed degradation. To eliminate this possibility, the reaction was quenched with exactly 2 equiv of either H_2SO_4 or HCl dissolved in Et_2O at –78 °C, followed by stirring of the mixture at –78 °C for 30 min. Filtration of the reaction mixture through celite removed undissolved solids.



1 or **2**

3 R = Et 81%
4 R = *i*-Pr 76%

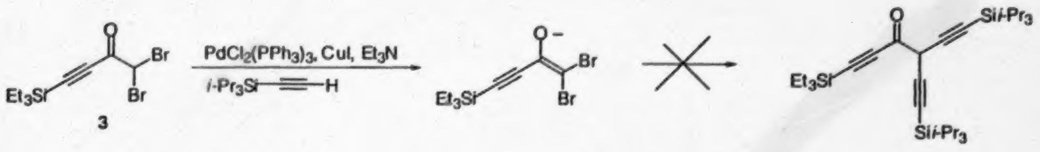
Scheme 3. Formation of Dibromides

After workup of the reaction mixture by either solvent evaporation or aqueous workup, results were similar. We found that quick filtration of the impure oil through a plug of silica gel, eluting with hexanes, was necessary to prevent further product degradation. Using the optimized procedure, ketone **3** was obtained in 81% yield. With the reaction conditions established for the TES protected compound, the more robust TIPS protected compound was predicted to be stable to these conditions. It was indeed found that the *i*-Pr_3Si protected **2** could be quenched with conc. aq HCl to afford ketone **4** in a yield of 76%. This is a quick reaction, requiring only a few hours to conduct, and it can be done on large quantities (6 g). The dibromide products are not light sensitive and can be stored under refrigeration for several months without decomposition.

1.1 Enolate Derivatives

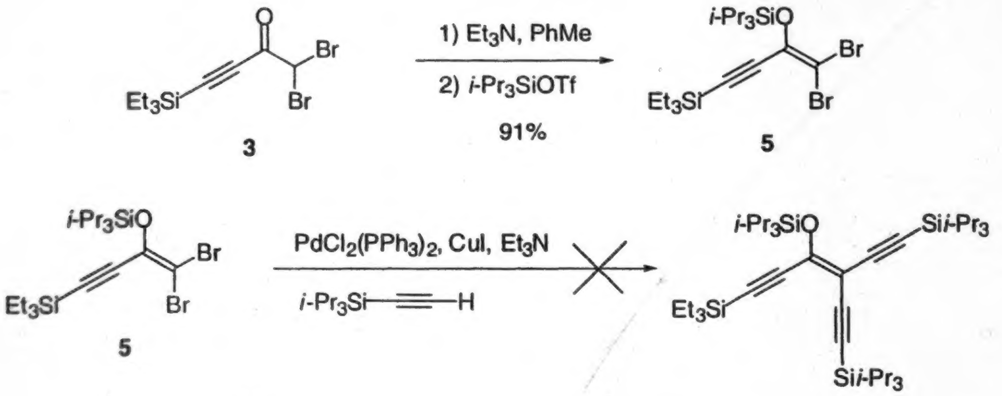
By far the easiest route to derivatizing the dibromides **3** and **4** would be accomplished via cross-coupling to the vinyl bromide of an in situ formed enolate.

Initial attempts at this failed when using the Sonogashira reaction (Scheme 4). The enolate may be too electron rich for oxidative addition of the palladium catalyst into the carbon-bromide bonds to occur. We decided that if the enolate were trapped as a silyl enol ether, we would be able to evaluate the potential of the dibromo-olefin to react by a palladium catalyzed cross-coupling reaction.



Scheme 4. Attempted Cross-Coupling of Ketone 3

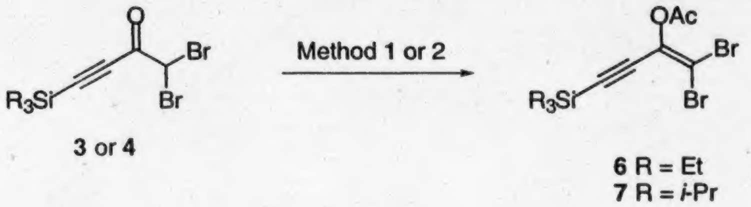
Treatment of compound **3** with Et_3N in toluene, and trapping with *i*-Pr_3SiOTf gave the enol ether **5** in good yield (91%) (Sceme 5). This silyl enol ether was tested for cross-coupling reactivity using the Sonogashira reaction, but yielded no positive results. It is known that the Sonogashira reaction is retarded by electron donating substituents on the halide substrate. It may be that the oxidative addition of palladium does not proceed in this electron rich silyl protected species.[15]



Et3Si
Br
Br
3
1) Et3N, PhMe
2) i-Pr3SiOTf
91%
i-Pr3SiO
Br
Et3Si
Br
5
i-Pr3SiO
Br
Et3Si
Br
5
PdCl2(PPh3)2, CuI, Et3N
i-Pr3Si—≡—H
i-Pr3SiO
Si-i-Pr3
Et3Si
Si-i-Pr3

Scheme 5. Attempted Silyl Enol Ether Cross-Coupling

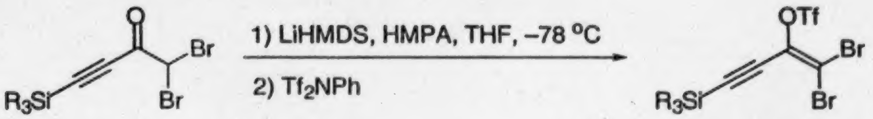
Two methodologies were employed to trap the dibromo-ketone **3** as an enol acetate (Scheme 6) while compound **4** was derivatized by one method. Using LiHMDS to effect enolate formation at –78 °C in THF, subsequent trapping with Ac_2O yielded the TES protected enol acetate **6** in 97% yield and the TIPS protected enol acetate **7** in 99% yield (method 1).[61] A somewhat easier route to the acetate was devised, using Et_3N in THF, followed by trapping of the enolate with Ac_2O aided by DMAP. This is a high yielding room temperature reaction for compound **6** with only a slight decrease in yield to 89%.[62] Both methods can be used in sufficient scale to prepare large quantities (4-6 g) of the acetates. The ease of method 2 and the speed at which it can be completed makes these conditions favorable to method 1. The reactivity of these acetates towards various cross-coupling methodology will be discussed in Section 1.2.



Method 1) LiHMDS, THF, –78 °C, then Ac_2O. R = Et (**6**) 97%, R = *i*-Pr (**7**) 99%.
Method 2) Et_3N, THF, DMAP, Ac_2O. R = Et (**6**) 89%.

Scheme 6. Formation of Dibromo-acetates

We envisioned that conversion of the dibromo ketones **3** and **4** to vinyl triflates could also lead to interesting compounds. Standard conditions for vinyl triflate formation developed by Stang using lutidine and triflic anhydride yielded no product.[49] Varying the experimental conditions by attempting the reaction at reflux was not successful. Also, using LDA or DMAP as the base did not effect product formation. We found that triflate formation was possible by using LiHMDS in THF at –78 °C to deprotonate, with HMPA present in the solution to generate a more naked enolate.[63] This methodology, using *N*-phenyltriflimide as a mild triflate source, produced high yields of both silyl protected triflates **8** and **9** (eq 21). It was surprising to find that such highly functionalized compounds were stable for weeks under refrigeration.



(21)

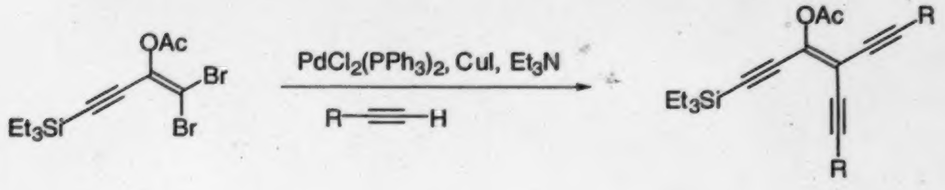
3 or **4**

8 R= Et 86%
9 R= *i*-Pr 70%

1.2 Sonogashira Cross-Coupling of Vinyl Acetate 6

Using vinyl acetate **6**, triethynyl derivatives were the first target molecules via palladium catalyzed cross-coupling reactions. Sonogashira cross-coupling is often used for the incorporation of an alkyne moiety. The base required for this type of cross-coupling reaction is usually a secondary or tertiary amine. In this case, a tertiary amine was used, as a secondary amine might cleave the acetate moiety. The Sonogashira methodology was attempted with $PdCl_2(PPh_3)_2$ and $Pd(PPh_3)_4$ as catalysts. The reactions of various alkynes and **6** with $PdCl_2(PPh_3)_2$ in neat triethylamine were complete within 24-36 h at rt and gave good yields. If the reaction is done at higher temperatures, a decreased yield is observed. The products from the Sonogashira reaction are shown below (Table 2). A variety of functional groups were successfully incorporated, including trialkylsilyl, aryl and ferrocenyl.

Table 2. Products of the Sonogashira Reaction with Vinyl Acetate 6



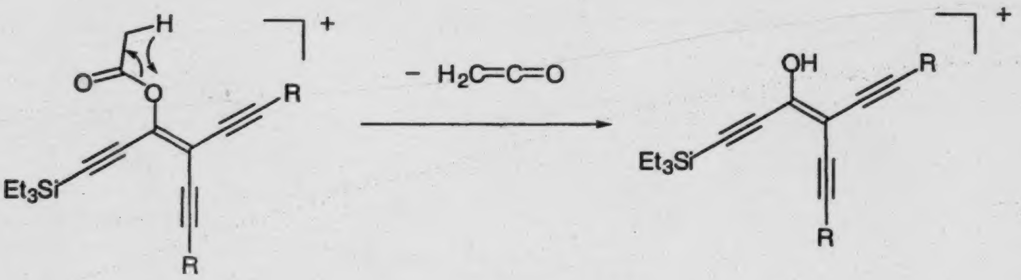
6

10 - 14

	R	Yield (%)
10	$SiMe_3$	55
11	$Si\textit{i}\text{-}Pr_3$	66
12	Phenyl	66
13	2-Naphthyl	66
14	Ferrocenyl	62

Spectroscopically, the ferrocenyl substituted compound **14** had one coincident carbon signal in the ^{13}C NMR spectrum, while the naphthyl appended **13** had two coincident carbon signals in the ^{13}C NMR spectrum. Despite the similar chemical structures and electronic environments in this series of triethynyl vinyl actetates, all six sp-hybridized carbon resonances were otherwise clearly observed for each compound. Interestingly, we noted that the chemical shifts of the sp^2 carbon resonances do not shift considerably between compounds.

The EI mass spectral characterization of these products revealed an $[M - 42]^+$ base peak for all triethynyl acetates. We suggest that the pathway for this fragmentation is loss of the acetate group with proton transfer to the oxygen (Scheme 7),[64] which eliminates the neutral ketene molecule.



Scheme 7. Fragmentation Pathway of Vinyl Acetates

Triethynyl compounds **11**,**12**, and **14** are stable for weeks under refrigeration. The naphthyl and the trimethylsilyl derivatives **10** and **13**, respectively, show limited stability, and decompose over several days. Despite precautions to retard this degradation, TMS derivative **10** was stable only long enough to be characterized. Triethynyl compounds **10-13** are oils, whereas the ferrocenyl compound **14** is a highly crystalline red solid. Crystallization by slow evaporation from dichloromethane afforded crystals suitable for X-ray analysis, and the ORTEP drawing is shown below in Figure 7. Even though sterically unencumbered, the ferrocenyl ligands are not coplanar with the rest of the conjugated framework. Rather, these moieties are twisted out of this planarity by 35.6° and 34.2°, for Fe2 and Fe1 respectively.

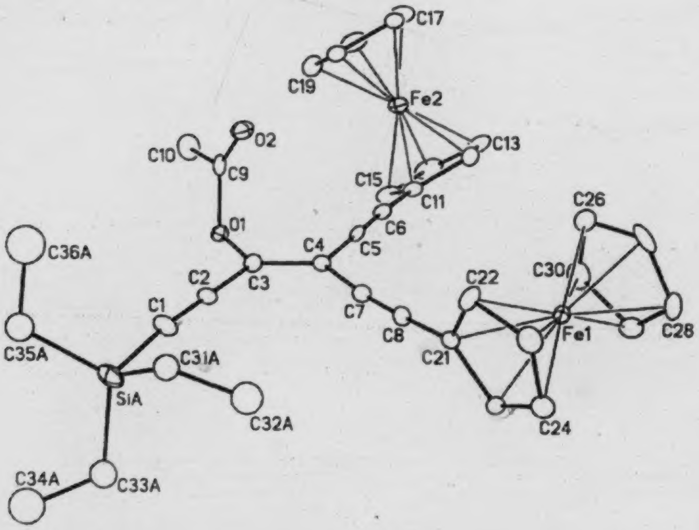
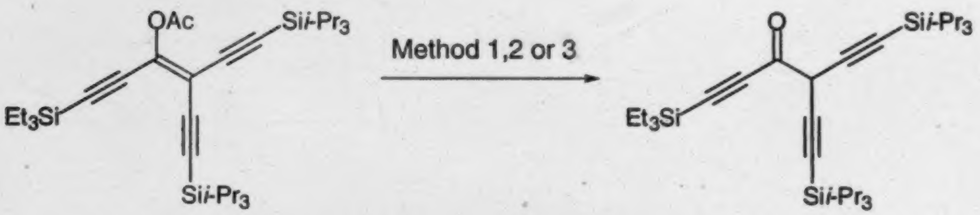

C17
C19
Fe2
C13
C10
O2
C9
C15
C11
C26
O1
C6
C36A
C4
C5
C2
C3
C22
C30
C1
C7
C8
Fe1
C28
C35A
C21
C31A
SiA
C32A
C24
C34A
C33A

Figure 7. ORTEP Drawing of Triethynyl Acetate 14

1.3 Removal of Acetate Protecting Group and Triflate Formation

With methodology established for the synthesis of triethynyl compounds such as **10-14**, formation of the corresponding ketones was examined. We predicted that once formed, the ketones could be derivatized to yield a variety of useful building blocks. For example, these compounds could in principle be converted to a vinyl triflate, which would enable further cross-coupling reactions to be accomplished on the triethynylethene core.

It was decided that the TIPS protected triethynyl derivative **11** would be used for the evaluation of a suitable vinyl acetate to vinyl triflate protocol. This compound is very stable and can be synthesized in good yield. A variety of methods were attempted for the removal of the acetate group, among them, $Mg(OMe)_2$, MeLi, and KCN in EtOH (Scheme 8).[65]

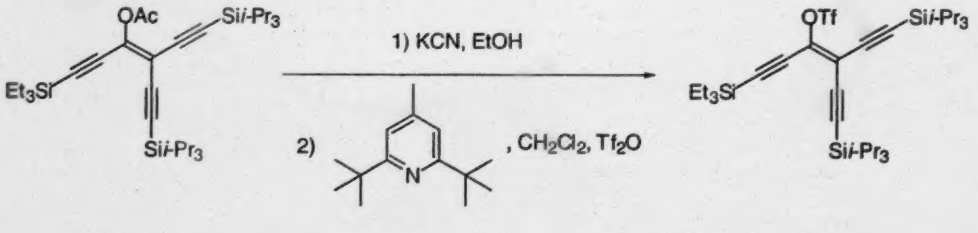


11

Method 1: 2 equiv MeLi, –78 °C, THF.
Method 2: $Mg(OMe)_2$, MeOH.
Method 3: 2 mol% KCN, EtOH.

Scheme 8. Deprotection of Vinyl Acetate 11

All routes led to the same result, the ketone could be generated but then decomposed, affording several byproducts. Monitoring the reaction by TLC, one main product would form, but, upon workup, decomposition resulted. The by-products were too unstable to characterize. The formation of the desired ketone was established through evidence such as its IR spectrum, noting the appearance of a ketone stretch at around 1720 cm^{-1} and the disappearance of the ester stretch at 1785 cm^{-1}. Interestingly, we noted the presence of an allenic stretch in the IR spectrum at approximately 1915 cm^{-1} as the ketone decomposed. The instability of the ketone product may result from Michael addition or Aldol chemistry. Despite precautions to protect the ketone from water, air, and light, the compound would degrade. Since deprotection to yield a stable triethynyl ketone product seemed impossible, we explored other methodology to derivatize the triethynyl compounds. The triflate would be the primary target. Acetate removal of **11** using KCN in EtOH, followed by quick addition of the ketone to a solution of base and triflic anhydride in CH_2Cl_2 yielded a modest 42% of the desired triflate **15** (equation 22). The fact that triflate **15** could be isolated confirmed that the ketone product is somewhat stable for a short period of time. In an attempt to increase the yield of this process, we decided to trap the enolate intermediate *in situ*.



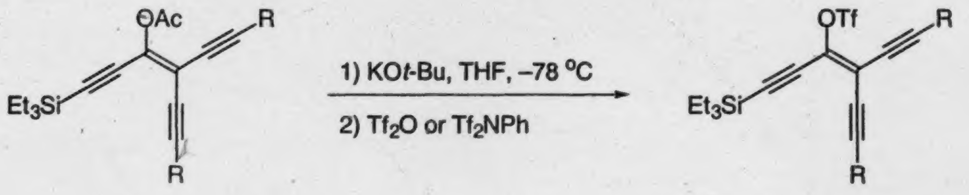
11

15

(22)

It has been reported in literature that enolates derived from enol acetates can be captured by electrophiles.[66] Although this process had not been established for the synthesis of vinyl triflates, to the best of our knowledge, it was expected to be possible. The triethynyl derivatives **11-14** were thus subjected to this approach by attempting to capture the enolate as a triflate. Using KO*t*-Bu in THF at -78 °C or -40 °C, followed by trapping with either Tf_2O or Tf_2NPh resulted in poor yields of the desired triflates (Table 3). The exception is the ferrocenyl substituted compound **18** at 77% yield. The intermediate ketone derived from **18** may be too sterically bulky to participate in aldol chemistry.

Table 3. Vinyl Triflate Formation Using KO*t*-Bu

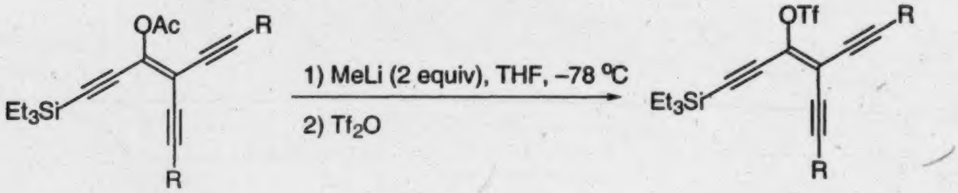


11-14 **15-18**

	R	Yield (%)
15	Si*i*-Pr$_3$	40
16	Phenyl	50
17	Naphthyl	37
18	Ferrocenyl	77

An alternate route for this transformation was evaluated with the intention of generating higher yields. Literature protocol employed MeLi for the removal of acetyl groups, with the resultant enolate being trapped by a variety of electrophiles.[50] For the conversion to the desired triflates, optimized conditions were established by employing 2 equiv of MeLi in THF at –78 °C, with stirring for 1 h, followed by trapping with triflic anhydride (Table 4). This procedure resulted in overall better yields.

Table 4. Triethynyl Triflate Formation Using MeLi



11,12,14 **15,16,18**

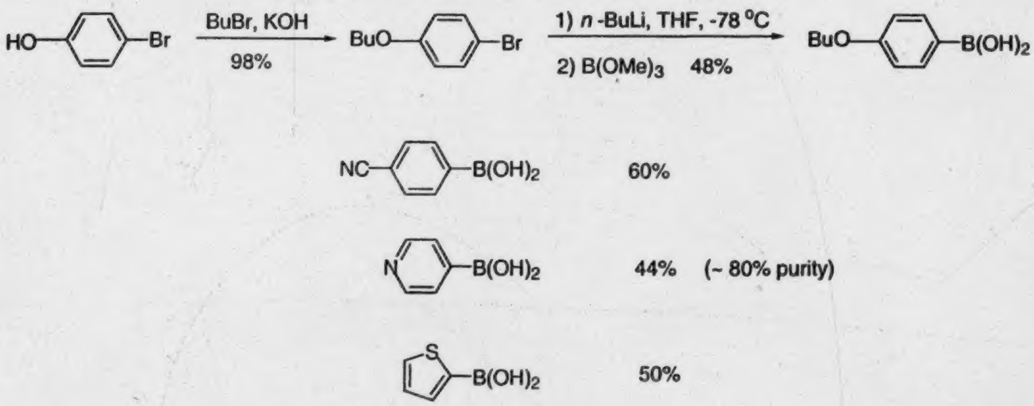
	R	Yield (%)
15	Si*i*-Pr$_3$	81
16	Phenyl	60
18	Ferrocenyl	72

The most distinctive spectral feature in the characterization of **15-18** were the quartets observable in the ^{13}C NMR spectrum for each compound. This is evidence of carbon fluorine coupling with $^{1}J_{CF}$ ~320 Hz, indicating that the transformations were successful. The ferrocenyl triflate **18** had 2 coincident carbon resonance peaks by ^{13}C NMR spectroscopy, otherwise all spectral data was consistent with the proposed structures.

1.4 Suzuki Cross-Coupling Reactions using Vinyl Acetate 6

Successful Sonogashira reactions with **6** established that the dibromo-olefin moiety could be elaborated via palladium catalyzed methods. Based on literature precedent, we expected that boronic acids would be viable organometallic coupling partners for **6** using the Suzuki cross-coupling protocol. The problem associated with Suzuki methodology is that a strong base is commonly utilized in the reaction. In the present case, this would remove both base labile protecting groups, *i.e.* the Et_3Si and Ac moieties. There is literature precedent, however, for the derivitization of base sensitive compounds in Suzuki reactions. One such method involves suspending a carbonate base in toluene, which we felt might be compatible with the substrate **6**.[22]

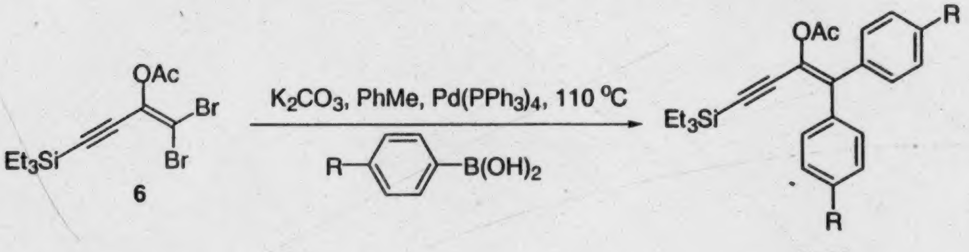
To evaluate the effectiveness of the Suzuki coupling of **6**, a series of boronic acids were synthesized. A boronic acid containing a solubilizing group was targeted first. Starting with 4-bromophenol, 4-bromobutoxybenzene was synthesized using KOH in butylbromide. This aryl alkoxide was then reacted with butyllithium to effect lithium-halogen exchange and trimethylborate was then added.[67] Following a basic work up that consisted of extracting the boronic acid into NaOH, acidifying and back-extracting into Et_2O, the butoxy substituted boronic acid was isolated in 48% yield (Scheme 9).[68] This compound, as suggested by ^1H NMR spectroscopic analysis, was quite pure. A heteroaromatic compound, 2-thiophene boronic acid,[69] and an electron withdrawing compound, p-cyanophenyl boronic acid,[70] were synthesized using the same methodology. Although we attempted the synthesis of 4-pyridyl boronic acid,[71] only small amounts of impure product could be isolated.



Scheme 9. Synthesis of Boronic Acids

Evaluation of the Suzuki protocol was done using the TES protected acetate **6** and commercially available *p*-tolyl boronic acid in toluene with potassium carbonate. The reaction was complete in 12 hours at reflux using 2.2 equiv of the boronic acid and $Pd(PPh_3)_4$ as the catalyst (Table 5). A comparison of sodium and potassium carbonate revealed that the latter was slightly more effective. To remove water, which could cleave both the silyl and acetate protecting groups under these conditions, the carbonate bases were dried prior to use in the Suzuki reactions using a drying pistol filled with methanol. Also noteworthy was that a considerable rate decrease occurred when $PdCl_2(PPh_3)_2$ was used as the catalyst for this transformation. The Suzuki reaction was then tested for its generality with the dibromide **6** using other boronic acids (Table 5).

Table 5. Products of the Suzuki Reaction with Vinyl Acetate 6



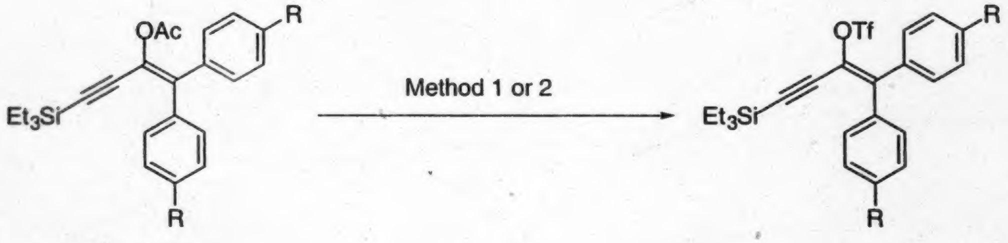
19-22

	R	Yield (%)
19	H	63
20	Me	69
21	OMe	50
22	OBu	85

The butoxy derivative **22** was synthesized in excellent yield. It is interesting that the other alkoxy substituted compound, anisyl derivative **21**, was only obtained in 50% yield. The difference may lie in the fact that the work up in the preparation of the butoxy substituted boronic acid used strong base (30% w/v NaOH), which may have resulted in less dimerized boronic acids present in the product. To evaluate this possibility, the other boronic acids could be subjected to this basic wash.

The thiophene boronic acid was unreactive to this procedure, using either the boronic acid synthesized in house or a sample purchased from Aldrich. The 4-cyanophenyl boronic acid was also unreactive under the weakly basic conditions used. The final boronic acid tested was the 4-pyridyl derivative, and as it was slightly impure, the negative results for this substrate were not unexpected. As the above results show, the reaction works well with simple alkyl or alkoxy substituted boronic acids. To date, however, other functional groups have not been as well-tolerated by this methodology. Nontheless, compounds **19-22** are quite easy to generate and purify. Using the optimized conditions for the conversion of vinyl acetates to triflates as described for **15**, **16**, and **18**, the diaryl acetates **19-22** were converted to vinyl triflates **23-26** in good to excellent yields (Table 6).

Table 6. Diaryl Vinyl Triflates



19-22 **23-26**

	R	Method	Yield (%)
23	H	Method 1	67
24	Me	Method 2	63
25	OMe	Method 1	65
26	OBu	Method 2	70

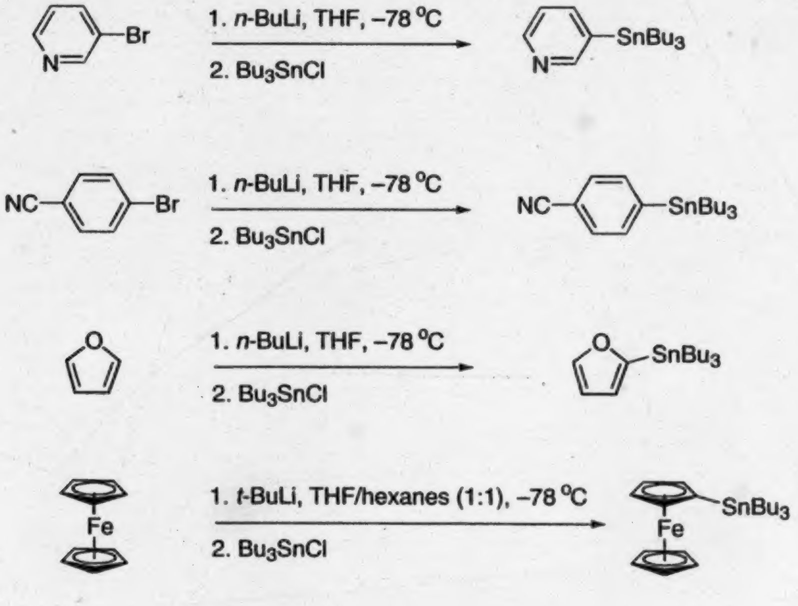
Method 1. 2 equiv MeLi, –20 °C, 1 h then Tf_2O
Method 2. 2 equiv MeLi, –78 °C, 1 h then Tf_2O

Although the synthesis of diphenyl triflate **23** has been previously described, the reported route used an expensive hindered base, required 5-7 days for completion, and afforded low yields of ~50%. The process outlined above involves only 1 h to react the acetate with MeLi and 30 min for reaction with the triflic anhydride to yield the product. Thus, the new method is more expeditious and provides better yields.

1.5 Stille Cross-Coupling of Vinyl Acetate 6

To synthesize some of the vinyl triflate derivatives that were inaccessible through the Suzuki transformation, we anticipated that an organostannane would be an effective cross-coupling partner. An advantage to the Stille reaction is that there is no base required, enabling simpler conditions to be utilized than in the Suzuki transformation.

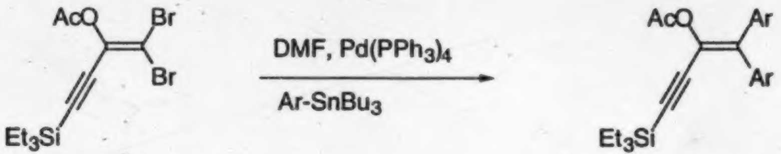
To synthesize the necessary stannanes, an aryl or heteroaryl bromide was treated first with *n*-BuLi in THF at –78 °C, then reacted with tributyltinchloride. After workup, the stannane products were approximately 90% pure, as judged by ^{1}H NMR spectroscopy. The 3-pyridyl and 4-cyanophenyl stannanes were synthesized in this manner (Scheme 10). The transformation of furan to the tributyltin derivative was achieved by way of direct lithiation of furan with *n*-BuLi and then quenching with tributyltinchloride.[72] Ferrocene required a stronger base and an unusual solvent system,[73] *t*-BuLi was added to ferrocene dissolved in a mixture of hexanes/THF (to solvate ferrocene), followed by quenching of the ferrocenyl anion with tributyltinchloride, which yielded the impure ferrocenylstannane. Purification required distillation at reduced pressure. These relatively simple reactions generated a broad series of organostannanes in relatively little time.



Scheme 10. Synthesis of Stannanes

The Stille reaction was first attempted using THF, $Pd(PPh_3)_4$ and 2,2'-dithiophenestannane.[74] After 3 days at reflux, the reaction was complete, yielding 24% of the desired product **28**. By employing NMP or DMF as solvent, and heating at 110 °C, reaction time was reduced to 2 h, leading to an increased yield of 50%. As the reaction proceeded more cleanly in DMF, this solvent was used in subsequent reactions (Table 7). Using this method, the 2-thienyl and 2-furanyl products **27** and **29** respectively, were synthesized. Although the successful formation of **28** seemed to solve the synthetic problems that had appeared in the case of the Suzuki reaction, tin residues made purification problematic. In certain cases the products had to be chromatographed several times to achieve acceptable levels of purity.

Table 7. Products from the Stille Reaction with Vinyl Acetate 6



6

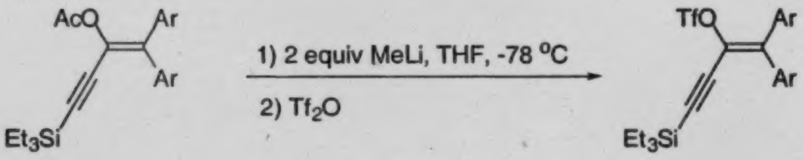
27-29

	Ar	Yield (%)
27	2-thienyl	66
28	2,2'-dithienyl	50
29	2-furanyl	57

Several stannanes were found to be unreactive under our modified conditions. In the case of the ferrocene, steric constraints may have been unfavorable, although there was no evident formation of even the mono-substituted compound. This would have been easy to see, as ferrocenyl substituted compounds are colored on TLC. The 3-pyridyl and the 4-cyanophenyl stannanes were also found to be unreactive.

Conversion of **27-29** to the triflates **30-32** was accomplished without difficulty (Table 8). This general procedure provides a route to novel heteroaromatic derivatized vinyl triflates. The 2-thienyl compound was converted in 85% yield, a significantly better yield than obtained for the others. The strongly basic conditions using MeLi are potentially not as compatible with the other heteroaryl groups, which may deprotonate or coordinate the Li cation, thus lowering the isolated yield.

Table 8. Heteroaryl Vinyl Triflates



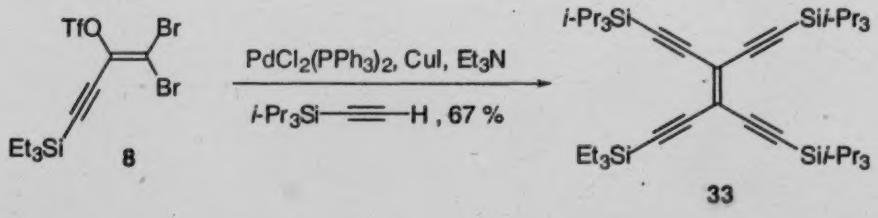
27-29 **30-32**

	Ar	Yield (%)
30	2-thienyl	85
31	2,2'-dithienyl	60
32	2-furanyl	57

1.6 Reactions of Vinyl Triflates

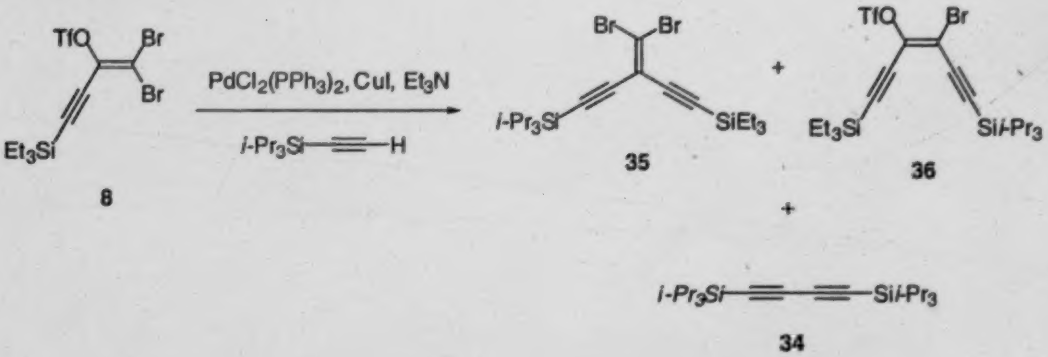
1.6.1 Dibromo-olefinic Vinyl Triflate 8

The reactivity of vinyl triflate **8** was explored with the intent of chemoselectively cross-coupling an alkyne to the vinyl triflate moiety. It was anticipated that this could be possible since vinyl bromides are usually slightly less reactive toward palladium catalyzed cross-coupling than vinyl triflates. The reactivity of the vinyl triflate was evaluated using the Sonogashira protocol. By conducting this reaction in the presence of excess triisopropylsilyl acetylene, the tetraethynyl ethene **33** was obtained (eq 23). The structure was verified by mass spectral data and ^{1}H NMR spectroscopy. This compound was previously synthesized by Diederich *et al.*[75]



(23)

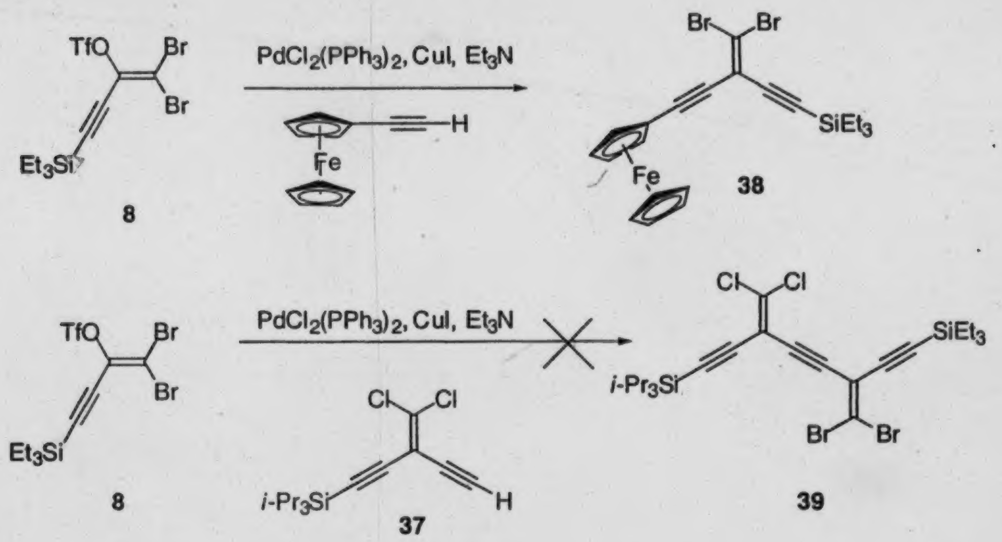
Using 1-1.5 equivalents of the TIPS acetylene was predicted to moderate the cross-coupling reaction and leave the vinyl halide moieties intact. Conditions of the Sonogashira reaction were then varied, including a change of solvent to THF, Et_3N, or DMF. The substrate was unstable in DMF, and THF and Et_3N did not afford any reaction. Also, changing the base (Et_2NH, i-Pr_2NH, or Et_3N) did not promote the reaction. In most cases the starting material was recovered, as well as what appeared to be dimerized acetylene, which results from oxidative homocoupling of the terminal alkynes. Mass spectral analysis of what appeared to be dimerized acetylene **34** revealed that the desired dibromo ene-diyne compound **35** did form, along with the other possible cross-coupled products such as **36** (Scheme 11).



Scheme 11. Attempted Chemoselective Cross-Coupling of Vinyl Triflate 8

Attempting to purify the desired product was difficult due to the non-polar nature of all of the compounds. Analysis of the ^1H NMR spectra revealed that the TIPS signal dominated the spectrum and the TES proton signal was essentially hidden in the baseline. Stopping the reaction after 30 min or 1-2 h yielded approximately the same mixture of products. It seems evident that the reactivity difference between the vinyl bromide or the vinyl triflate is not effectively different. As such, the possibility for selective cross-coupling at the vinyl triflate position currently remains difficult, if not impossible.

The Sonogashira reaction of **8** was also attempted with dichloro ene-diyne **37** (synthesized from compound **45**) and ferrocenyl acetylene (Scheme 12). In both cases, the reaction seemed to stop midway, as determined by TLC analysis. The ferrocenyl product **38** was isolated in 15% yield, as determined by ^1H NMR spectroscopic analysis. The triyne **39** was not isolated. The addition of more terminal acetylene or fresh catalyst did not enable the reaction to proceed any further. These results are unusual, as vinyl triflates are normally quite successful as cross-coupling partners. It is certainly worthwhile to investigate possible chemoselective cross-coupling to the triflate **8** by utilizing other cross-coupling methodology, but to date the necessary conditions remain unrealized.

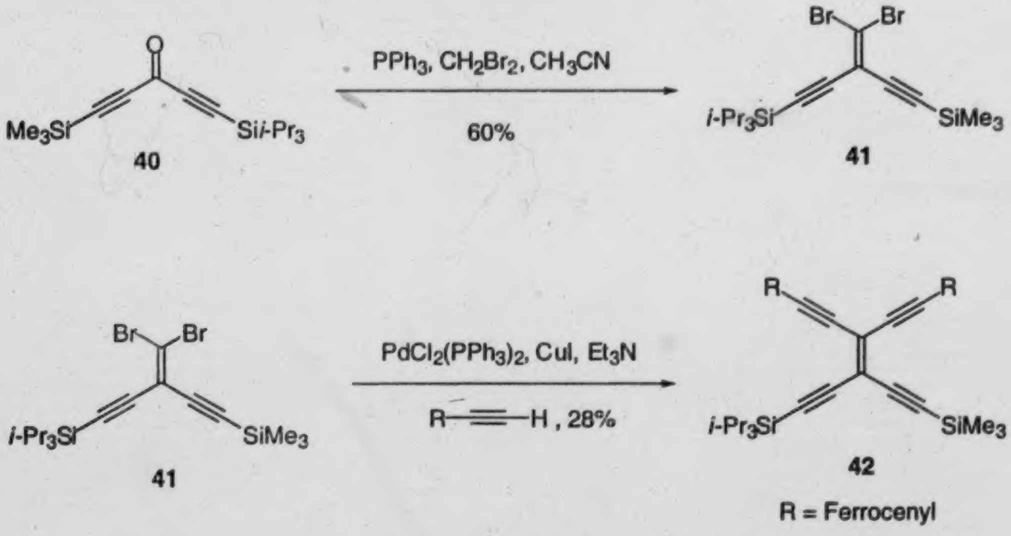


TfO
Br
Br
Et3Si
8
PdCl2(PPh3)2, CuI, Et3N
H
Fe
Br
Br
SiEt3
Fe
38
TfO
Br
Br
Et3Si
8
PdCl2(PPh3)2, CuI, Et3N
Cl
Cl
i-Pr3Si
H
37
Cl
Cl
SiEt3
i-Pr3Si
Br
Br
39

Scheme 12. Reactions of Vinyl Triflate 8

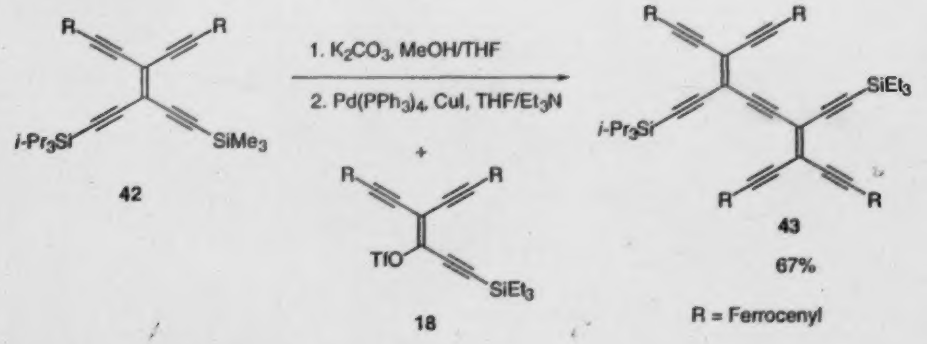
1.6.2 Synthesis of an Oligomer

The vinyl triflates generated by the methodology described in previous sections 1.2-1.5 have the potential to be utilized in the synthesis of oligomers or macrocycles. To evaluate this possibility, one such example was attempted. The ferrocenyl endcapped triethynyl triflate **18** (p. 45) was thought to be a good starting point. The assembly of a monomer for reaction with **18** was the only other necessary step. Using diethynyl ketone **40**, Corey-Fuchs dibromo-olefination[76] in acetonitrile proceeded in good yield to produce compound **41** as previously reported.[77] The resulting dibromide **41** was then subjected to palladium catalyzed cross-coupling with ethynylferrocene to give a differentially protected tetraethynylethene (compound **42**, Scheme 13).


Me3Si
Si*i*-Pr3
40
PPh3, CH2Br2, CH3CN
60%
Br
Br
i-Pr3Si
SiMe3
41
Br
Br
i-Pr3Si
SiMe3
41
PdCl2(PPh3)2, CuI, Et3N
R—≡—H , 28%
R
R
i-Pr3Si
SiMe3
42
R = Ferrocenyl

Scheme 13. Synthesis of a Monomer

Compound **42** was then selectively deprotected with K_2CO_3 in wet MeOH/THF, and, following workup, the free alkyne was added to a solution of the triflate **18** in Et_3N/THF. The solution was degassed, $Pd(PPh_3)_4$ and CuI were added, and the reaction stirred for 24 h at rt. Workup and chromatography gave an acceptable yield of the small oligomer **43** (eq 24). Characterization of this oligomer was difficult, as several carbon resonances overlapped in the ^{13}C NMR spectrum. Nontheless, all characteristics, including mass spectral data and ^1H NMR spectroscopy, were consistent with those expected for the product **43**. It is evident that these functionalized vinyl triflates can be incorporated into larger structures.



R
R
i-Pr3Si
SiMe3
42
1. K2CO3, MeOH/THF
2. Pd(PPh3)4, CuI, THF/Et3N
+
R
R
TfO
SiEt3
18
R
R
SiEt3
i-Pr3Si
R
R
43
67%
R = Ferrocenyl

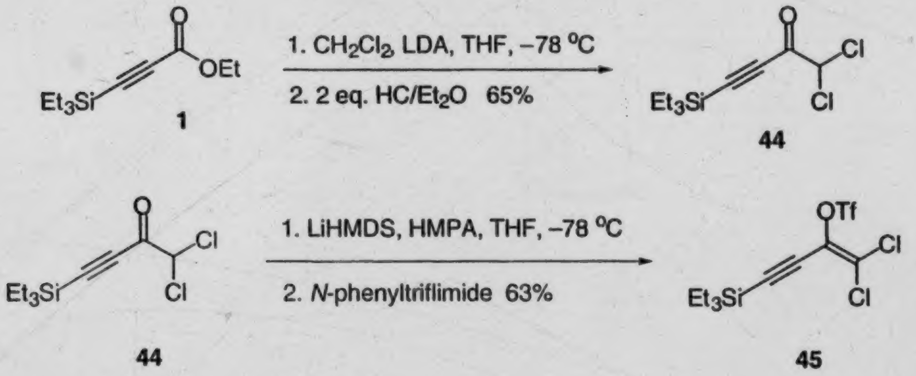
(24)

2 Chlorinated Derivatives

2.1 Synthesis

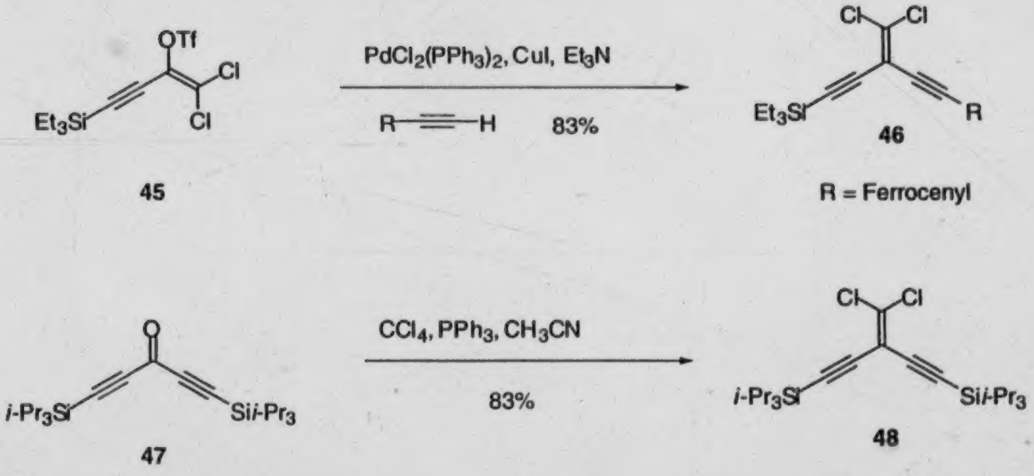
As discussed previously, the vinyl triflate **8** could not be derivatized chemoselectivly at the triflate moiety via palladium catalyzed Sonogashira reactions. We thought that the analogous chlorinated compound could be synthesized using the same methodology. The expected advantage of a dichloro analogue was that the carbon-chlorine bond is much stronger than a carbon-bromine bond, and the cross-coupling reaction to these centers would be much less favored. This methodology would allow for chemoselective cross-coupling to the vinyl triflate moiety.

Using the triethylsilyl protected ester **1**, reaction with dichloromethane under the conditions previously optimized for **3** led to the dichloroketone **44** in 65% yield. This compound was then converted to the vinyl triflate **45** in good yield using LiHMDS as the base and *N*-phenyltriflimide as the triflate source (Scheme 14).


Et3Si
OEt
1
1. CH2Cl2, LDA, THF, –78 °C
2. 2 eq. HC/Et2O 65%
Et3Si
Cl
Cl
44
Et3Si
Cl
Cl
44
1. LiHMDS, HMPA, THF, –78 °C
2. N-phenyltriflimide 63%
OTf
Et3Si
Cl
Cl
45

Scheme 14. Synthesis of Dichloro Vinyl Triflate 45

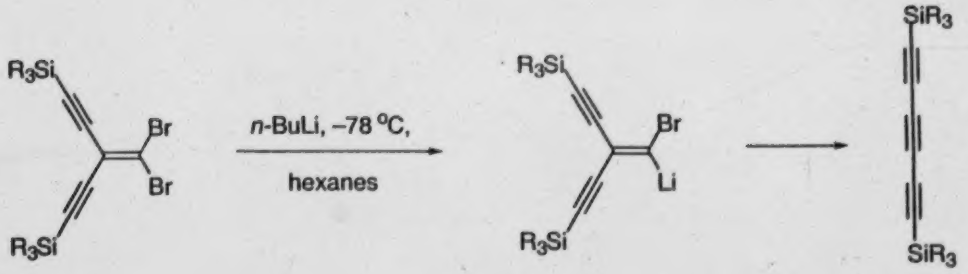
To examine the possibility of a chemoselective reaction, the vinyl triflate **45** was cross-coupled with ethynylferrocene, $PdCl_2(PPh_3)_4$, and CuI in Et_3N to yield **46** (Scheme 15). As the synthesis for the dichloro-olefin **46** was several steps, a simpler route to a dichloro-olefin compound was also explored. Using diethynyl ketone **47**, dichloro-olefination using CCl_4 and triphenylphosphine in CH_3CN afforded compound **48** in good yield.


OTf
Cl
Cl
Et3Si
45
PdCl2(PPh3)2, CuI, Et3N
R—≡—H
83%
Cl
Cl
Et3Si
R
46
R = Ferrocenyl
O
i-Pr3Si
Si/-Pr3
47
CCl4, PPh3, CH3CN
83%
Cl
Cl
i-Pr3Si
Si/-Pr3
48

Scheme 15. Synthesis of Dichloro-olefinic Compounds

2.2 Rearrangement Evaluation

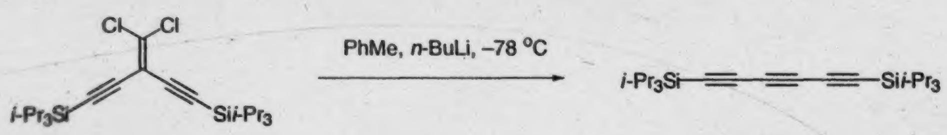
It has been established that dibromo-olefinic compounds appended with alkynes can undergo a carbenoid rearrangement to yield triynes.[78] This is analogous to the Fritsch-Buttenberg-Weitchell rearrangement of diaryl dibromo-olefins.[79] The rearrangement is thought to proceed via lithium-halogen exchange and subsequent carbene or carbenoid rearrangement to yield the alkyne (Scheme 16). This is an efficient way to incorporate an alkyne unit when other routes are difficult.



Scheme 16. Rearrangement of Dibromo-olefinic Compounds

We anticipated that a similar rearrangement could be accomplished on the dichloro compounds such as **46** or **48**. The analogous dibromide compound to dichloride **48** had been previously synthesized and rearranged to yield the triyne. Using this triyne for comparison, we evaluated the possible rearrangement reactions of **48**. The most common methodology for evaluation purposes was either ^{13}C NMR spectroscopic analysis or mass spectral analysis.

Evaluation of the standard conditions for the transformation of **48** to **49** (eq 25), *n*-BuLi in hexanes at –78 °C, resulted in no product formation. We varied the solvent, employing Et_2O, THF, benzene, and toluene. Of these solvents, Et_2O and THF led to the mono protonated product, as well as recovered starting material in approximately equal quantities. This was verified by mass spectral data and ^{1}H NMR spectroscopic analysis. In benzene and toluene, *n*-BuLi effected formation of the product **49** in approximately 30% yield.



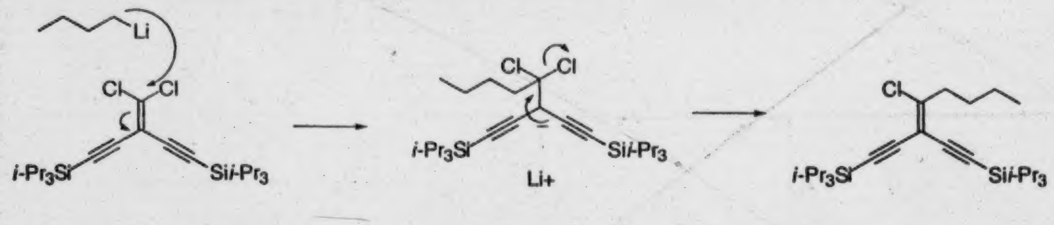
48

49

(25)

The reaction progressed more cleanly in toluene, most likely due to the fact that lower temperatures can be used with toluene as the solvent. Rearrangement was incomplete using conditions of 1-1.5 equiv of *n*-BuLi, with slow warming of the mixture from –78 °C to –40 °C, or to rt. It was anticipated that the base could be altered, in type or amount, to effect complete transformation. Using *n*-BuLi at 3 or more equivalents, the reaction was still incomplete, with formation of rearranged product and the butylated derivative **50**. The structure of this byproduct was suggested by mass spectral data and ^{1}H NMR spectroscopic analysis. If left overnight, the products/starting materials would decompose under the reaction conditions. Formation of the butylated derivative **50** can be accounted for via two possible routes. If the lithium-halogen exchange was occurring, the resultant intermediate was stable enough to react subsequently with butylchloride.

Conversely, we suspect it is also possible that the *n*-BuLi may act as a nucleophile, with subsequent elimination of the chloride anion (Scheme 17).



48 **50**

Scheme 17. Formation of Butylated Byproducts

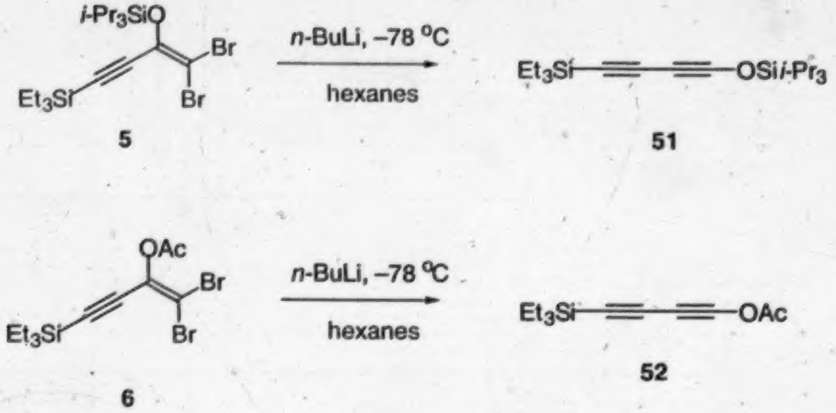
To eliminate the possibility that the vinyl lithium intermediate was reacting with butylchloride, inverse addition was attempted. Adding the dichloro-olefin to a solution of excess of *n*-BuLi, we predicted that the butylchloride would react with excess *n*-BuLi, leaving the reaction intermediate free to rearrange. This was not the case, however, as decomposition occurred and no starting material or product was recovered.

A more hindered base, such as *t*-BuLi, was anticipated to halt the formation of the undesired by-products. This base would allow the lithium-halogen exchange to occur, and the chlorinated byproduct *t*-BuCl would not be subject to nucleophilic attack. Using *t*-BuLi at 1-1.5 equiv in toluene at –78 °C did indeed effect triyne formation (~40%), but the reaction did not reach completion. Adding an excess of base caused degradation of the material.

Evaluation of the rearrangement of dichloro-olefin compounds revealed that although these precursors do have the ability to rearrange in a manner analogous to the dibromides, the reaction is not as facile. The chloride anion is known to be an inferior leaving group compared to a bromide anion. This attribute may hinder the intermediate carbene/carbenoid species from rearrangement and, in fact, lead to a more nucleophilic characteristic of the intermediate vinyl lithium species.

3. Rearrangement of Dibromide Derivatives

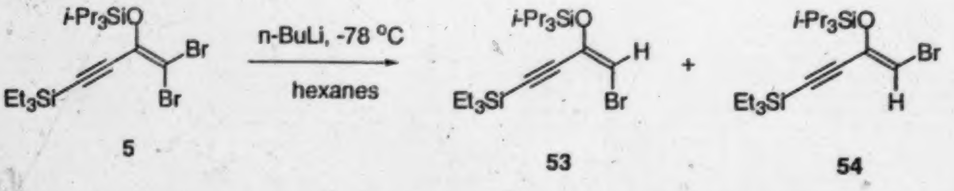
The silyl enol ether **5** and enol acetate **6** were possible precursors for alkynyl ethers or esters like **51** or **52**, respectively, by way of a carbenoid rearrangement (Scheme 18). There are few known methods for the synthesis of these types of interesting molecules.[80] If there were an alternative route for their synthesis as simple as this rearrangement, this would be of great synthetic utility.



i-Pr3SiO
Br
Br
Et3Si
5
n-BuLi, –78 °C
hexanes
Et3Si
OSi i-Pr3
51
OAc
Br
Br
Et3Si
6
n-BuLi, –78 °C
hexanes
Et3Si
OAc
52

Scheme 18. Alkynyl Ethers and Esters

Compounds **5** and **6** were thus evaluated for their potential to undergo rearrangement. Treatment of the silyl enol ether with *n*-BuLi in hexanes at –78 °C yielded both protonated products **53** and **54** upon workup (equation 26). Changing the solvent to THF, Et_2O, or benzene yielded similar results. The protonated starting material was evident in all trials, without any evidence of diyne formation.



i-Pr3SiO
Br
Br
Et3Si
5
n-BuLi, -78 °C
hexanes
i-Pr3SiO
H
Br
Et3Si
53
+
i-Pr3SiO
Br
H
Et3Si
54

(26)

The ester **6** was also subjected to rearrangement conditions of *n*-BuLi in hexanes at –78 °C, which resulted in decomposition of the starting material. No product or starting material was recovered upon reaction workup. Several possible reactions could occur at the ester moiety upon addition of *n*-BuLi, such as deprotonation of the ester or nucleophilic attack. The starting material was thus found to be unsuitable for this rearrangement.

III CONCLUSIONS

Methodology for the synthesis of a variety of functionalized vinyl triflates has been developed. Using this methodology, a series of alkynyl, aryl, and heteroaryl vinyl triflates were synthesized. These building blocks were demonstrated to be applicable to the synthesis of oligomeric compounds, as suggested by the synthesis of the small oligomer **43**. In a comparison of methodology, the Suzuki cross-coupling was found to be the most easily adaptable. The starting materials for the Suzuki reaction were easily synthesized in most cases, and the products were highly stable.

Additional derivatives remain to be synthesized, as intended for specific research goals. Ligands that contain electron withdrawing groups or pyridyl groups would be particularly useful. These ligands can probably be incorporated into the vinyl triflates through the use of biaryl type boronic acids. By placing the EWG or pyridyl moiety further from the boronic acid reaction center, the cross-coupling might be successfully achieved.

Alternatively, boronic acids could be synthesized with other EWG, such as fluorinated benzene. Compounds such as isoquinoline or phenanthroline may also be incorporated instead of the pyridyl group. It should be added, however, that it has not yet been determined if the boronic acids containg the cyanophenyl or pyridyl moiety were unreactive due to functional group incompatibility or limited purity of these boronic acids. As pyridyl boronic acids are very difficult to purify, utilizing an alternate group with similar functional attributes may yield boronic acids that could be purified more easily.

The vinyl triflates that have been successfully generated can be incorporated into macrocycles and oligomers. The alkoxy substituted vinyl triflate **26** or similar derivatives should provide solubility to the desired macromolecules, enabling larger derivatives to be assembled. An interesting area for investigation involving these alkoxy substituted vinyl triflates would be the incorporation of glycol type alkoxy chains. Side chains such as these may lead to liquid crystal properties being exhibited by the macrocyclic structures.

IV EXPERIMENTAL SECTION

General. Reagents were purchased reagent grade from commercial suppliers and used without further purification. 1-Naphthyl acetylene,[81] phenylacetylene,[82] ferrocenylacetylene,[83] 4-butoxyphenyl boronic acid,[68] 2-thiophenyl boronic acid,[69] 4-cyanophenyl boronic acid,[70] 4-pyridyl boronic acid,[71] 2-thiophenyl tributylstannane,[53] 2,2'-bithiophenyltributylstannane,[53] furanyltributylstannane,[84] 3-pyridyltributylstannane,[84] 4-cyanophenyltributylstannane,[85] and diethynyl ketones **40**[77] and **47**[86] were prepared as previously reported. Evaporation and concentration *in vacuo* were done at H_2O-aspirator pressure. All reactions were performed in standard, dry glassware under an inert atmosphere of Ar unless otherwise stated. Flash column chromatography[87]: *silica gel-60* (230-400 mesh) from *General Intermediates of Canada.* Thin Layer Chromatography (TLC): plastic sheets coated with silica gel-60 F_{254} with the fluorescent indicator UV_{254} from Macherey-Nagel; visualization by UV light or $KMnO_4$ stain. Mp: Fisher-Johns melting point apparatus; uncorrected. IR spectra (cm^{-1}): *Nicolet Magna-IR 750.* ^1H and ^{13}C NMR: *Bruker AM-300, Varian Inova 300, 400, 500 or Varian Unity 500* instruments, at rt in $CDCl_3$ (sovent peaks: 7.24 ppm for ^1H and 77.0 ppm for ^{13}C as reference) or CD_2Cl_2 (solvent peaks: 5.3 ppm for ^1H and 53.1 ppm for ^{13}C as reference) or $(CD_3)_2CO$ (solvent peaks: 2.05 ppm for ^1H and 29.8 and 206.3 ppm for ^{13}C as reference). EIMS: *Kratos MS-50* instrument, peaks as *m/z*. ESIMS: *Micromass Zabspec Hybrid Sector-TOF*, in either positive or negative ion mode, peaks as *m/z*. X-ray crystallographic analysis was done on a Siemens P4/RA X-ray diffractometer by Meitian Wang. Elemental analyses were performed by Spectral Services at the University of Alberta, using a *Carlo Era 1108 Elemental Analyzer*.

General Procedure for Sonogashira Cross-Coupling Reactions

To a degassed solution of dibromoacetate **3** and 3 equiv of the terminal acetylene in triethylamine were added $PdCl_2(PPh_3)_2$ (5 mol%), and CuI (10 mol%). The mixture was then stirred at rt for 1-3 days, and monitored by TLC. When complete, the reaction mixture was filtered through celite and diluted with Et_2O. The solution is washed with H_2O (10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. Compounds were isolated by silica gel column chromatography, typically eluted with mixtures of hexanes and Et_2O.

General Procedure for Suzuki Cross-Coupling Reactions

To a dry, degassed solution of the dibromoacetate **3** and 2.2 equiv of the boronic acid in toluene were added 2.2 equivalents K_2CO_3 and $Pd(PPh_3)_4$ (5 mol%). The mixture was then heated to reflux for 6-12 hr until judged complete, as monitored by TLC. The mixture was then filtered through celite and diluted with Et_2O. The organic layer was washed with H_2O (2 x 10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. Compounds were isolated by silica gel column chromatography, typically eluted with mixtures of hexanes and Et_2O.

General Procedure for Stille Cross-Coupling Reactions

To a degassed solution of the dibromoacetate **3** and 2.2 equiv of the stannane in DMF was added $Pd(PPh_3)_4$ (5 mol%). The mixture was then heated to 120 °C for 2 - 4 h and monitored by TLC. The mixture was then cooled to rt, poured into H_2O (10 mL) and diluted with Et_2O. The organic layer was washed with brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was then purified by silica gel column chromatography, typically eluted with mixtures of hexanes and Et_2O.

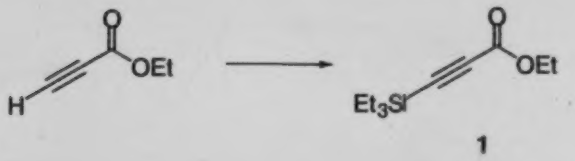
General Procedure for Triflate Formation

The vinyl acetate compound was dissolved in THF and cooled to –78 °C. To this was added 2 equiv of MeLi (1.6 M in Et_2O). The mixture was then stirred at –78 °C for 1 h. To the mixture was then added 2 equiv of Tf_2O. The reaction was typically complete within 20 min, at which time the mixture was poured into sat.

NH_4Cl (10 mL) and diluted with Et_2O. The organic layer was then washed twice with H_2O (2 x 10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. Compounds were purified by silica gel column chromatography, typically eluted with mixtures of hexanes and Et_2O.

General Procedure for LDA or LiHMDS Formation

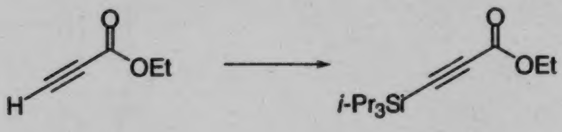
To a stirred solution of either *i*-Pr_2NH or HMDS in the appropriate solvent (THF or Et_2O) at –78 °C, was added 1 equiv *n*-BuLi. The mixture was stirred at –78 °C for 30 min and then added to reactions via cannula or syringe.



1

Triethylsilyl propynoic acid ethyl ester (1)

Ethyl propiolate (4.61 g, 47.0 mmol) in THF (40 mL) was cooled to –78 °C. To this was added LDA (47.0 mmol) in THF (40 mL) over 10 min. The mixture was stirred for 30 min at –78 °C, triethylsilyl chloride (7.08 g, 47.0 mmol) was added and the mixture allowed to warm to rt overnight. The mixture was poured into sat. NH_4Cl (30 mL), extracted with Et_2O (2 x 30 mL), and the organic layer washed with brine (30 mL), dried ($MgSO_4$), filtered, and evaporated. The residue was filtered through silica gel (hexanes) to yield **1** (9.36 g, 44.2 mmol, 94%) as a yellow oil. R_f = 0.7 (hexane/EtOAc 30:1). IR (neat) 2958, 2913, 2877, 2178, 1713, 1459 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.17 (q, *J* = 7.2 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H), 0.98 (t, *J* = 7.8 Hz, 9H), 0.66 (q, *J* = 7.8 Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$, APT) δ 153.1, 96.0, 91.7, 62.0, 14.0, 7.2, 3.8; EIMS *m/z* 212 (M^+, 27), 183 ($[M - Et]^+$, 100); HRMS calcd for $C_{11}H_{20}O_2Si$ (M^+) 183.0841, found 183.0844. Anal. calcd. for $C_{11}H_{20}O_2Si$: C, 62.21; H, 9.49. Found: C, 62.30; H, 9.79.

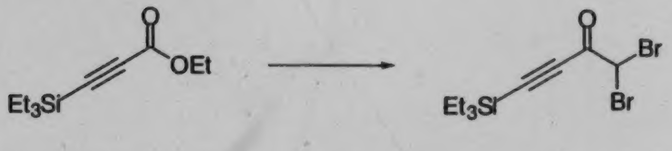


2

Triisopropylsilyl propynoic acid ethyl ester (2)

Ethyl propynoate (1.93 g, 19.6 mmol) in THF (20 mL) was cooled to –78 °C. To this was added LDA (19.7 mmol) in THF (20 mL) over 10 min. The mixture was then stirred at –78 °C for 30 min, triisopropylsilyltrifluoromethanesulfonate (6.04 g, 19.7 mmol) was added and the mixture allowed to warm to rt overnight. The mixture was poured into sat. NH_4Cl (30 mL), extracted with Et_2O (2 x 30 mL), and the organic layer washed with brine (30 mL), dried ($MgSO_4$), filtered, and evaporated. The residue was filtered through silica gel (hexanes) to yield **2** (4.69

g, 18.5 mmol, 94%) as a colorless oil. $R_f = 0.6$ (hexane/Et_2O 10:1). IR (CH_2Cl_2, cast) 2945, 2893, 2867, 2177, 1713, 1463, 1385, 1366 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.21 (q, $J = 7.2$ Hz, 2H), 1.29 (t, $J = 7.2$ Hz, 3H), 1.05-1.11 (m, 21H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 153.1, 96.9, 90.8, 61.9, 18.5, 14.1, 11.0; EIMS *m/z* 254 (M^+, 20), 211 ($[M - i\text{-}Pr]^+$, 100); HRMS calcd. for $C_{14}H_{26}O_2Si$ (M^+) 254.1702, found 254.1704.

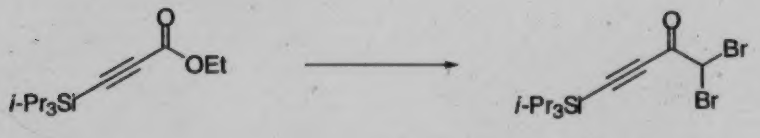


1 3

1,1-Dibromo-4-triethylsilyl-but-2-one-3-yne (3)

To a stirred solution of dibromomethane (0.331 mL, 4.72 mmol) and compound **1** (500 mg, 2.32 mmol) in Et_2O (10 mL) at –78 °C was added a solution of LDA (4.72 mmol) in Et_2O (10 mL) over a period of 5 min. The mixture was stirred for 20 min at –78 °C and then hydrolyzed with H_2SO_4 (0.25 mL) in Et_2O (2 mL). The mixture was stirred for 30 min at –78 °C and then filtered through celite. The solution was evaporated and passed through a plug of silica gel (hexanes) to yield **3** (638 mg, 1.88 mmol, 81%) as a light yellow oil. $R_f = 0.5$ (hexane/EtOAc 30:1). IR (neat) 3014, 2957, 2936, 2912, 2875, 2156, 1685, 1457, 1413 cm^{-1}; ^1H

NMR (300 MHz, $CDCl_3$) δ 5.83 (s, 1H), 1.03 (t, *J* = 8.1, 9H), 0.70 (q, *J* = 8.1, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$, APT) δ 173.0, 104.9, 97.6, 42.2, 7.3, 3.8; EIMS *m/z* 339 (M$^+$, 4), 167 ([M - $CHBr_2$]$^+$, 100); HRMS calcd. for $C_{10}H_{16}O^{79}Br^{81}BrSi$ (M$^+$) 339.9317, found 339.9315. Anal calcd for $C_{10}H_{16}OBr_2Si$: C, 35.31; H, 4.74. Found: C, 35.49; H, 4.95.

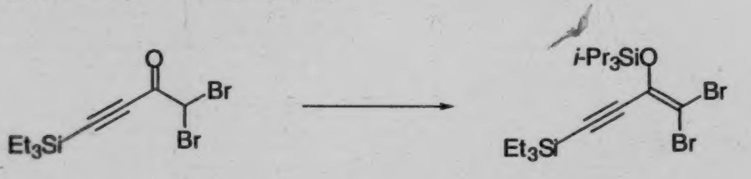


2 4

1,1-Dibromo-4-triisopropylsilyl-but-2-one-3-yne (4)

To a stirred solution of dibromomethane (0.240 mL, 3.38 mmol) and compound **2** (430 mg, 1.69 mmol) in Et_2O (10 mL) at –78 °C was added a solution of LDA (3.38 mmol) in Et_2O (10 mL) over a period of 5 min. The mixture was stirred for 20 min at –78 °C and then hydrolyzed with HCl (5 mL, 6M). The organic layer was washed with 10% $NaHCO_3$ (20 mL), brine (30 mL), dried ($MgSO_4$), filtered, and evaporated. The residue was passed through a plug of silica gel (hexanes/Et_2O 30:1) to yield **4** (493 mg, 1.15 mmol, 76%) as a light yellow oil. R_f = 0.5 (hexane/EtOAc 20:1). IR (neat) 3015, 2944, 2891, 2867, 2155, 1684, 1462, 1385, 1368 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.83 (s, 1H), 1.08-1.21 (m, 21H);

^{13}C NMR (75.5 MHz, CDCl$_3$, APT) δ 172.9, 104.3, 98.3, 42.3, 18.5, 11.0; EIMS *m/z* 381 (M$^+$, 9), 209 ([M - CHBr$_2$]$^+$, 100); HRMS calcd. for $C_{13}H_{22}OSi^{79}Br^{81}Br$ (M$^+$) 381.9786, found 381.9778.



3

5

1,1-Dibromo-4-triethylsilyl-2-triisopropylsilyloxy-but-1-en-3-yne (5)

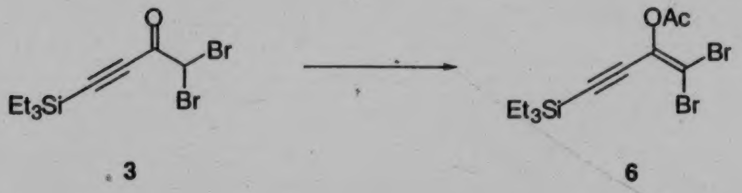
To a solution of **3** (200 mg, 0.59 mmol) in toluene (4 mL) at rt was added Et$_3$N (89 mg, 0.88 mmol). The mixture was stirred for 15 min and triisopropylsilyltrifluoromethanesulfonate (198 mg, 0.647 mmol) was added. After 30 min the mixture was diluted with Et$_2$O (10 mL), washed with sat. NH$_4$Cl (10 mL), dried (MgSO$_4$) filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc 10:1) to yield **5** (266 mg, 0.540 mmol, 91%) as a colorless oil. R$_f$ = 0.7 (hexane/EtOAc 10:1). IR (neat) 2956, 2869, 2732, 2150, 1555, 1462, 1413, 1384, 1368 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.26-1.40 (m, 3H), 1.13 (d, *J* = 7.2 Hz, 18H), 1.04 (t, *J* = 8.0 Hz, 9H), 0.68 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (75.5 MHz, CDCl$_3$, APT) δ 136.2, 101.8, 99.4, 85.5, 17.9, 12.8, 7.3, 4.1; EIMS *m/z* 496 (M$^+$, 19), 424 ([M – Et - *i* -Pr]$^+$, 100);

HRMS calcd. for $C_{19}H_{36}OSi_2{}^{79}Br^{81}Br$ (M^+) 496.0650, found 496.0653. Anal. Calcd. for $C_{19}H_{36}OSi_2Br_2$,: C, 45.97; H, 7.31. Found: C, 46.36; H, 7.59.

Attempted Rearrangement of Silyl Enol Ether 5

Silyl enol ether **5** (100 mg, 0.22 mmol) was dissolved in hexanes (5 mL) and cooled to –78 °C. To this was added *n*-BuLi (0.89 mL, 0.24 mmol) and the mixture stirred at –78 °C for 30 min. The mixture was warmed to rt, poured into H_2O (10 mL), and diluted with Et_2O (10 mL). The organic layer was washed with brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et_2O 20:1) to yield a mixture of protonated products **53** and **54**. These products were characterized by mass spectral analysis and ^1H NMR spectroscopy.

Other attempted methods: *n*-BuLi in THF or Et_2O, effecting similar mixtures.

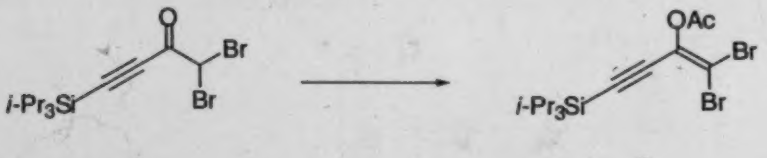


2-Acetoxy-1,1-dibromo-4-triethylsilyl-but-1-en-3-yne (6)

Compound **3** (457 mg, 1.34 mmol) in THF (10 mL) was cooled to –78 °C, LiHMDS (1.61 mmol) in THF (5 mL) was added and the mixture stirred for 30 min at –78 °C. Ac_2O was added (0.190 mL, 206 mg, 2.02 mmol) and the mixture allowed to warm to rt over a period of 4 h. The mixture was quenched with sat. NH_4Cl (10 mL), extracted with Et_2O (2 x 20 mL), and the organic layer was washed with brine (20 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by filtration through a plug of silica gel (hexane/Et_2O 20:1) to yield **6** (499 mg, 1.31 mmol, 97%) as an amber oil. $R_f = 0.3$ (hexane/Et_2O 30:1). IR ($CHCl_3$, cast) 2956, 2912, 2875, 2735, 2150, 1783, 1711, 1575, 1457, 1414 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.19 (s, 3H) 0.98 (t, $J = 7.8$ Hz, 9H) 0.62 (q, $J = 7.8$ Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$, APT) δ 166.3, 133.2, 104.1, 96.7, 95.6, 20.5, 7.4, 4.0; EIMS *m/z* 381 (M^+, 13), 339 ($[M - C_2H_2O]^+$, 100); HRMS calcd. for $C_{12}H_{18}{}^{79}Br^{81}BrO_2Si$ (M^+) 381.9435, found 381.9422. Anal. calcd. for $C_{12}H_{18}Br_2O_2Si$: C, 37.71; H, 4.75. Found: C, 37.99; H, 4.98.

Alternate procedure:

To a solution of **3** (1.38 g, 4.08 mmol) in THF (30 mL) was added Et_3N (0.85 mL, 620 mg, 6.10 mmol), then Ac_2O (0.960 mL, 1.04g, 10.2 mmol). The solution was stirred for 5 min, and DMAP (49.8 mg, 0.408 mmol) was added. After TLC analysis indicated completion (1 h) the mixture was poured into sat. NH_4Cl (20 mL), diluted with Et_2O (20 mL), the organic layer washed with brine (30 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by filtration through silica gel (hexane/Et_2O 20:1) to yield **6** (1.38 g, 3.62 mmol, 89%).

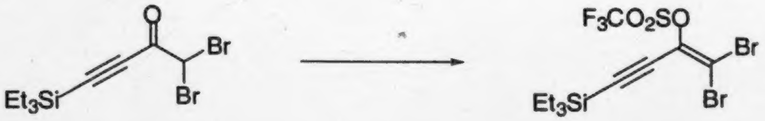


4 **7**

2-Acetoxy-1,1-dibromo-4-triisopropylsilyl-but-1-en-3-yne (7)

Compound **4** (400 mg, 1.05 mmol) in THF (10 mL) was cooled to –78 °C, LiHMDS (1.26 mmol) in THF (5 mL) was added and the mixture stirred for 30 min at –78 °C. Ac_2O was added (160 mg, 1.58 mmol) and the mixture allowed to warm to rt over a period of 4 h. The mixture was quenched with sat. NH_4Cl (10 mL) and extracted with Et_2O (2 x 20 mL). The organic layer was washed with brine (20 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by filtration through silica gel (hexane/Et_2O 20:1) to yield **7** (438 mg, 1.04 mmol, 99%) as an amber oil. $R_f = 0.5$ (hexane/Et_2O 15:1). IR (CH_2Cl_2, cast) 2944, 2891, 2866, 1784, 1711, 1463, 1367 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.19 (s, 3H), 1.02–1.14 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$, APT) δ 166.3, 133.3, 103.3, 97.4, 95.3, 20.4, 18.5, 11.0; EIMS *m/z* 423 (M^+, 7); HRMS calculated for

$C_{15}H_{24}O_2Si\ ^{79}Br^{81}Br$ (M^+) 423.9892, found 423.9879. EA attempted but unsuccessful.



3 8

1,1-Dibromo-4-triethylsilyl-2-trifluoromethanesulfoxy-but-1-en-3-yne (8)

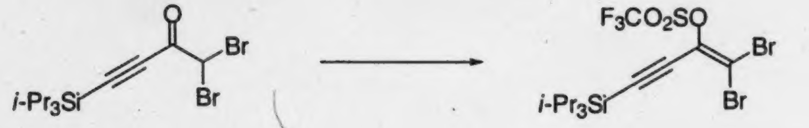
To a mixture of **3** (200 mg, 0.588 mmol) and HMPA (179 mg, 0.882 mmol) in THF (5 mL) at –78 °C was added LiHMDS (0.765 mmol) in THF (5 mL). The mixture was stirred at –78 °C for 30 min and *N*-phenyltriflamide (252 mg, 0.706 mmol) in THF (6 mL) was added. The solution was allowed to warm to rt over 3 h. Sat. NH_4Cl (10 mL) was added and the mixture was extracted with Et_2O (2 x 30 mL), the organic layer was washed with brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (hexanes) to give **8** (238 mg, 0.505 mmol, 86%) as a pale yellow oil. R_f = 0.8 (hexanes/Et_2O 30:1). IR (neat) 2959, 2914, 2878, 1457, 1423, 1249 cm^{-1}; ^1H NMR (300 MHZ, $CDCl_3$) δ 1.00 (t, J = 8.1 Hz, 9H), 0.66 (q, J = 8.1 Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$, APT) δ 131.7, 118.3 (q, J = 325 Hz, CF_3), 104.3, 100.6, 94.1, 7.3, 3.9; EIMS m/z 471 (M^+, 40); HRMS calcd. for

$C_{11}H_{15}O_3SiF_3S^{79}Br^{81}Br$ (M^+) 471.8799, found 471.8809. EA attempted but unsuccessful.

Attempted Cross-Couplings of Vinyl Triflate 8

Vinyl Triflate **8** (20 mg, 0.042 mmol) and triisopropylsilylacetylene were dissolved in Et_3N (5 mL), the solution degassed for 30 min, and $Pd(PPh_3)_4$ (2.5 mg, 0.002 mmol) and CuI (5 mg, 0.3 mmol) were added. The mixture was stirred for 2 h, poured into H_2O (5 mL), and diluted with Et_2O (10 mL). The organic layer was washed with brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. This yielded a mixture of products, inseparable by chromatography.

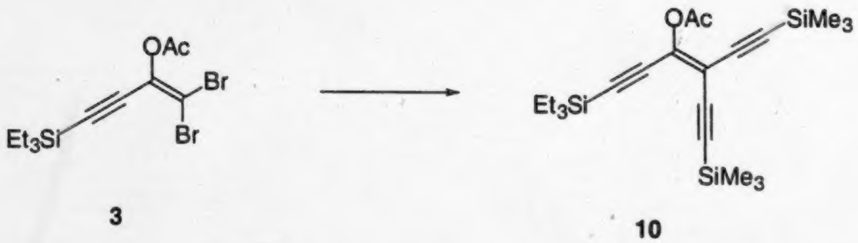
Other attempted conditions: $PdCl_2(PPh_3)_2$ in Et_3N yielded a mixture of products; $Pd(PPh_3)_4$ in DMF decomposed the vinyl triflate; $PdCl_2(PPh_3)_2$ in THF/Et_2NH or THF/*i*-Pr_2NH yielded mixtures of products.



4 **9**

1,1-Dibromo-2-trifluoromethanesulfoxy-4-triisopropylsilyl-but-1-en-3-yne (9)

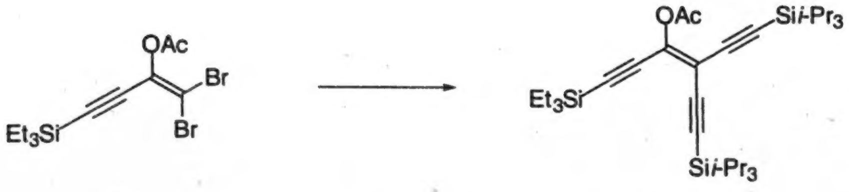
To a mixture of **4** (200 mg, 0.526 mmol) and HMPA (141 mg, 0.789 mmol) in THF (5 mL) at –78 °C was added LiHMDS (0.684 mmol) in THF (5 mL). The mixture was stirred at –78 °C for 30 min and *N*-phenyltriflamide (226 mg, 0.631 mmol) in THF (4 mL) was added. The solution was allowed to warm to rt over 3 h. Sat. NH_4Cl (10 mL) was added and the mixture was extracted with Et_2O (2 x 30 mL), the organic layer was washed with brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexanes) to give **9** (191 mg, 0.372 mmol, 70%) as a colorless oil. R_f = 0.7 (hexane/Et_2O 30:1). IR (neat) 2946, 2893, 2867, 1571, 1463, 1433, 1385, 1368 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.04-1.16 (m, 21H); ^{13}C NMR (75.5 MHz, $CDCl_3$, APT) δ 131.6, 118.2 (q, *J* = 321 Hz, *C*F_3), 108.8, 100.5, 94.8, 18.4, 11.0; EIMS *m/z* 513 (M^+, 22); HRMS calcd. for $C_{14}H_{21}O_3SiF_3S^{79}Br^{81}Br$ 513.9279, found 513.9273.



3 **10**

3-Acetoxy-1-triethylsilyl-4-trimethylsilylethynyl-6-trimethylsilyl-hex-3-en-1,5-diyne (10)

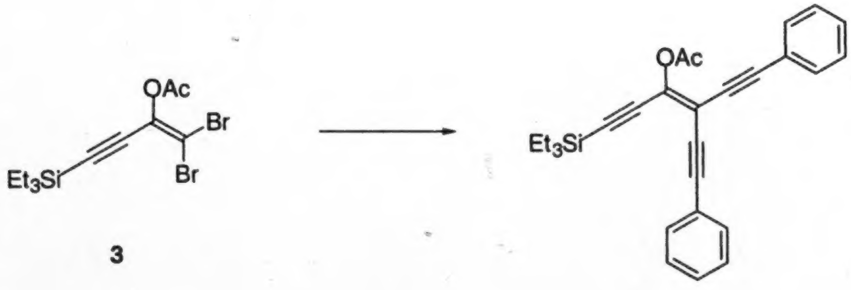
To a degassed solution of compound **3** (50 mg, 0.13 mmol) and trimethylsilylacetylene (64 mg, 0.66 mmol) in Et_3N (13 mL) was added $PdCl_2(PPh_3)_2$ (4.6 mg, 0.0066 mmol), and CuI (10 mg, 0.0053 mmol). The mixture was stirred at rt for 4 days, then filtered through celite and evaporated. The residue was diluted with Et_2O (10 mL), washed with H_2O (10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et_2O 40:1) to yield **10** (30 mg, 0.072 mmol, 55%) as a yellow oil. R_f = 0.4 (hexane/Et_2O 40:1); IR (CH_2Cl_2, cast) 2958, 2912, 2876, 2160, 1784, 1458, 1436, 1413, 1368 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.16 (s, 3H), 0.98 (t, *J* = 8.1 Hz, 9H), 0.63 (q, *J* = 8.1 Hz, 6H), 0.18 (s, 9H), 0.17 (s, 9H); ^{13}C NMR (75.5 MHz, $CDCl_3$, APT) δ 166.7, 143.1, 108.7, 106.8, 105.4, 105.0, 98.4, 98.1, 97.1, 20.6, 7.5, 7.4, 4.1, -0.3; EIMS *m/z* 416 (M^+, 10), 374 ($[M - C_2H_2O]^+$, 100); HRMS calcd. for $C_{22}H_{36}O_2Si_3$ (M^+) 416.2023, found 416.2016.



3 **11**

3-Acetoxy-1-triethylsilyl-4-triisopropylsilylethynyl-6-triisopropylsilyl-hex-3-en-1,5-diyne (11)

To a degassed solution of compound **3** (100 mg, 0.262 mmol) and triisopropylacetylene (238 mg, 1.31 mmol) in Et_3N (20 mL) was added $PdCl_2(PPh_3)_2$ (9.2 mg, 0.0013 mmol), and CuI (18 mg, 0.095 mmol). The mixture was stirred at rt for 3 days, then filtered through celite and evaporated. The residue was diluted with Et_2O (10 mL), washed with H_2O (10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et_2O 50:1) to yield **11** (101 mg, 0.173 mmol, 66%) as a yellow oil. $R_f = 0.5$ (hexane/Et_2O 40:1); IR (CH_2Cl_2, cast) 2943, 2865, 2159, 1785, 1463, 1414, 1383, 1367 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.15 (s, 3H), 1.07 (s, 21H), 1.04 (s, 21H), 0.96 (t, $J = 8.1$ Hz, 9H), 0.61 (q, $J = 8.1$ Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.9, 141.5, 106.4, 105.3, 101.2, 100.6, 99.8, 98.9, 98.4, 20.6, 18.6, 18.5, 11.4, 11.2, 7.4, 4.0; EIMS *m/z* 584 (M^+, 14), 542 ([M – $C_2H_2O]^+$, 100); HRMS calcd. for $C_{34}H_{60}O_2Si_3$ (M^+) 584.3901, found 584.3910. EA attempted but unsuccessful.



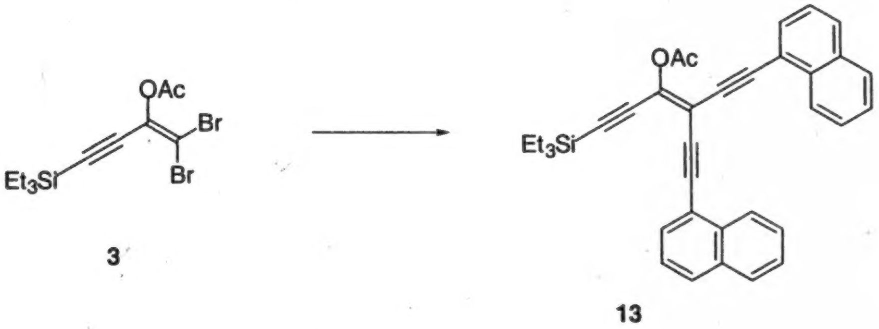
3

12

3-Acetoxy-4-phenylethynyl-6-phenyl-1-triethylsilyl-hex-3-en-1,5-diyne (12)

To a degassed solution of compound **3** (50 mg, 0.13 mmol) and phenylacetylene (114 mg, 0.654 mmol) in Et_3N (10 mL) was added $PdCl_2(PPh_3)_2$ (4.6 mg, 0.0066 mmol), and CuI (10 mg, 0.053 mmol). The mixture was stirred at rt for 24 h, then filtered through celite and evaporated. The residue was diluted with Et_2O (10 mL), washed with H_2O (10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et_2O 60:1) to yield **12** (37 mg, 0.087 mmol, 66%) as a light yellow oil. R_f = 0.4 (hexane/Et_2O 5:1). IR (CH_2Cl_2, cast) 3060, 2956, 2911, 2874, 2205, 2136, 1781, 1596, 1571, 1491, 1457, 1442, 1413 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.4-7.52 (m, 4H), 7.26-7.36 (m, 6H), 2.26 (s, 3H), 0.98 (t, J = 8.1 Hz, 9H), 0.65

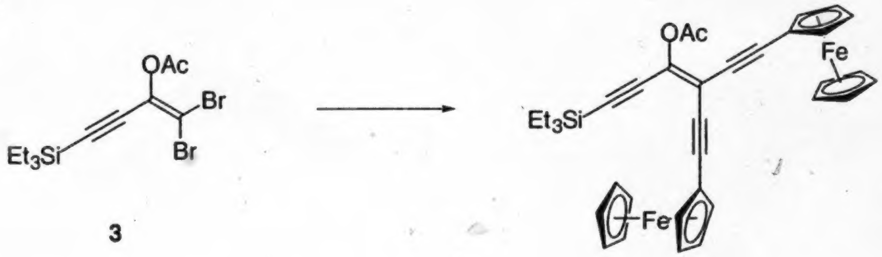
(q, $J = 8.1$ Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 167.1, 141.1, 131.8, 131.7, 129.1, 128.8, 128.4, 128.2, 122.6, 122.4, 106.8, 105.4, 99.1, 98.8, 95.0, 84.0, 82.8, 20.7, 7.5, 4.2; EIMS *m/z* 424 (M^+, 16), 382 ($[M - C_2H_2O]^+$, 100); HRMS calcd. for $C_{28}H_{28}O_2Si$ (M^+) 424.1859, found 424.1859.



3-Acetoxy-4-naphthylethynyl-6-naphthyl-1-triethylsilyl-hex-3-en-1,5-diyne (13)

To a degassed solution of compound **3** (50 mg, 0.131 mmol) and naphthylacetylene (147 mg, 0.654 mmol) in Et_3N (10 mL) was added $PdCl_2(PPh_3)_2$ (4.6 mg, 0.0066 mmol), and CuI (10 mg, 0.053 mmol). The mixture was stirred at rt for 48 h, then filtered through celite and evaporated. The residue was diluted with Et_2O (10 mL), washed with H_2O (10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et_2O 10:1) to give **13** (45 mg, 0.086 mmol,

66%) as an orange oil. R_f = 0.3 (hexane/Et_2O 10:1). IR (CH_2Cl_2, cast) 3057, 2955, 2910, 2874, 2194, 2135, 1781, 1585, 1545, 1506, 1460, 1403, 1368, 1333 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.1 Hz, 1H), 8.37 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 9.0 Hz, 4H), 7.77 (d, *J* = 7.2 Hz, 1H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.49-7.60 (m, 4H), 7.44 (t, *J* = 8.1 Hz, 2H), 2.32 (s, 3H), 0.98 (t, *J* = 7.8 Hz, 9H), 0.66 (q, *J* = 7.8 Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$, APT) δ 167.2, 140.6, 133.3, 133.2, 130.9, 130.8, 129.7, 129.5, 128.4, 128.3, 127.1, 127.0, 126.6, 126.5, 126.4, 126.0, 125.3, 125.2, 120.3, 120.1, 107.3, 105.5, 99.0, 97.4, 93.7, 88.8, 87.9, 20.8, 7.4, 4.2, (2 coincident signals); EIMS *m/z* 524 (M^+, 31), 482 ([M – $C_2H_2O]^+$, 100) ; HRMS calcd. for $C_{36}H_{32}O_2Si$ (M^+) 524.2171, found, 524.2168.

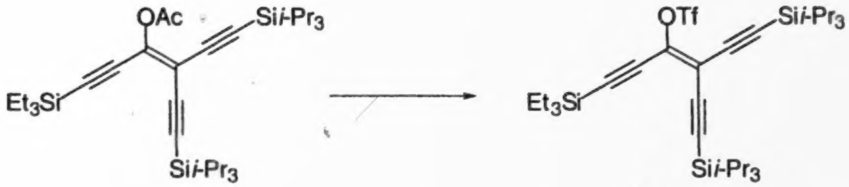


3

14

3-Acetoxy-4-ferrocenylethynyl-6-ferrocenyl-1-triethylsilyl-hex-3-en-1,5-diyne (14)

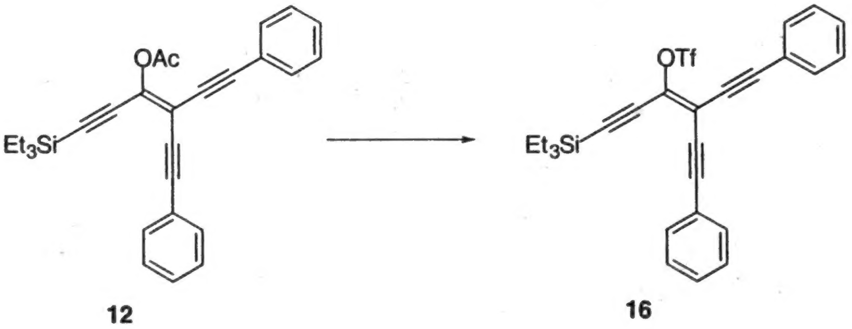
To a degassed solution of compound **3** (50 mg, 0.131 mmol) and ethynylferrocene (137 mg, 0.654 mmol) in Et_3N (10 mL) was added $PdCl_2(PPh_3)_2$ (4.6 mg, 0.0066 mmol), and CuI (10 mg, 0.053 mmol). The mixture was stirred at rt for 48 h, filtered through celite and evaporated. The residue was diluted with Et_2O (10 mL), washed with H_2O (10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et_2O 20:1) to yield **14** (52 mg, 0.081 mmol, 62%) as a red solid, Mp 89-91 °C. $R_f = 0.2$ (hexane/Et_2O 10:1). IR (CH_2Cl_2, cast) 3096, 2955, 2911, 2874, 2200, 2130, 1776, 1427, 1412, 1366, 1324 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.43-4.47 (m, 4H), 4.19-4.24 (m, 14H), 2.30 (s, 3H), 1.0 (t, $J = 7.5$ Hz, 9H), 0.67 (q, $J = 7.5$ Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$, APT) δ 167.1, 138.8, 106.4, 105.4, 99.5, 98.8, 94.9, 80.7, 79.7, 71.6, 70.2, 70.1, 69.4, 69.2, 64.4, 64.0, 20.8, 7.6, 4.3, (1 coincident signal); EIMS *m/z* 640 (M^+, 100); HRMS calcd. for $C_{36}H_{36}O_2SiFe_2$ (M^+) 640.1184, found 640.1168. EA attempted but unsuccessful. Crystals grown by slow evaporation of CH_2Cl_2 solution. For details of the X-ray crystallography see appendix.



11 **15**

1-Triethylsilyl-3-trifluoromethanesulfoxy-4-triisopropylsilylethynyl-6-triisopropylsilyl-hex-3-en-1,5-diyne (15)

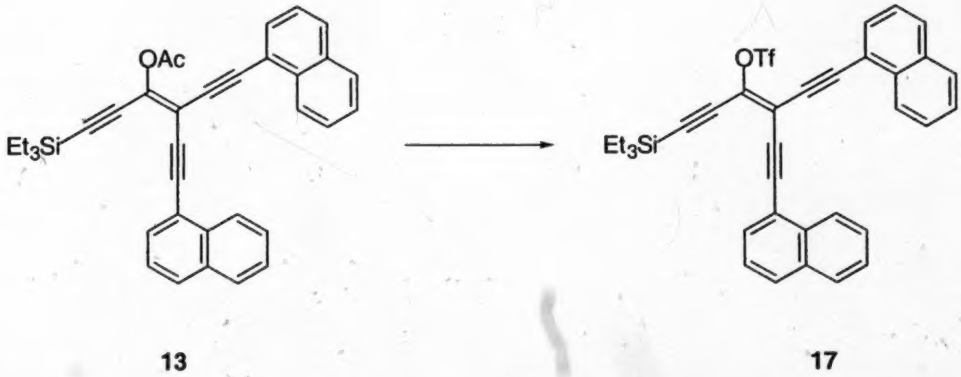
Compound **11** (118 mg, 0.202 mmol) was dissolved in THF (5 mL) and cooled to –78 °C. To this was added MeLi (0.25 mL, 0.40 mmol, 1.6 M in Et_2O). The mixture was stirred at –78 °C for 1 h, and Tf_2O (114 mg, 0.404 mmol) was added. The mixture was stirred for 20 min, poured into sat. NH_4Cl (10 mL) and diluted with Et_2O (10 mL). The organic layer was washed with H_2O (2 x 10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et_2O 10:1) to yield **15** (110 mg, 0.148 mmol, 81%) as a light yellow oil. $R_f = 0.5$ (hexane). IR ($CDCl_3$, cast) 2958, 2944, 2911, 2867, 1463, 1432, 1384, 1273 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.05-1.10 (m, 42H), 0.97 (t, $J = 8.1$ Hz, 9H), 0.64 (q, $J = 8.1$ Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.9, 118.4 (q, $J = 320$ Hz, CF_3), 111.3, 108.8, 106.8, 102.5, 99.3, 98.1, 95.8, 18.6, 18.5, 11.2, 11.1, 7.3, 3.9. EIMS *m/z* 674 (M^+, 66), 589 ([M – 2 *i*-Pr]$^+$, 100); HRMS calcd. for $C_{33}H_{57}F_3O_3SSi_3$ (M^+) 674.3289, found 674.3307. Anal. calcd. for $C_{33}H_{57}F_3O_3SSi_3$: C, 58.71; H, 8.51. Found: C, 58.78; H, 8.83.



12 **16**

4-phenylethynyl-6-phenyl-1-triethylsilyl-3-trifluoromethanesulfoxy-hex-3-en-1,5-diyne (16)

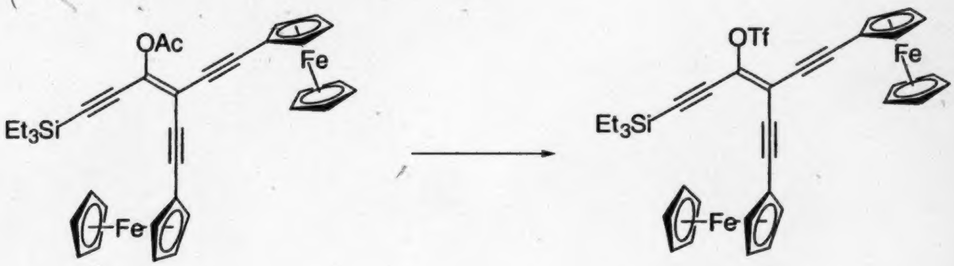
Compound **12** (60 mg, 0.17 mmol) was dissolved in THF (3 mL) and cooled to –78 °C. To this was added MeLi (0.21 mL, 0.34 mmol, 1.6 M in Et_2O). The mixture was stirred at –78 °C for 1 h, and Tf_2O (96 mg, 0.34 mmol) was added. The mixture was stirred for 20 min, poured into sat. NH_4Cl (10 mL) and diluted with Et_2O (10 mL). The organic layer was washed with H_2O (2 x 10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et_2O 10:1) to yield **16** (53 mg, 0.10 mmol, 60%) as a colorless oil. R_f = 0.6 (hexane/Et_2O 5:1). IR (CH_2Cl_2, cast) 3063, 2958, 2913, 2195, 2136, 1597, 1492, 1457, 1427, 1357, 1249 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.5-7.6 (m, 4H), 7.34-7.46 (m, 6H), 1.02 (t, *J* = 7.8 Hz, 9H), 0.71 (q, *J* = 7.8 Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 138.6, 132.3, 132.2, 130.3, 130.0, 128.97, 128.90, 121.9, 121.8, 118.8 (q, *J* = 321 Hz, CF_3), 112.3, 109.2, 102.6, 98.3, 96.4, 82.8, 82.0, 7.4, 4.3; EIMS *m/z* 514 (M^+, 23), 381 ($[M - SO_2CF_3]^+$, 100); HRMS calcd. for $C_{27}H_{25}F_3O_3SSi$ (M^+) 514.1243, found 514.1239.



4-Naphthylethynyl-6-naphthyl-3-trifluoromethanesulfoxy-1-triethylsilyl-hex-3-en-1,5-diyne (17)

Compound **13** (21 mg, 0.041 mmol) was dissolved in THF (3 mL) and cooled to –78 °C. To the solution was added KO*t*-Bu (4.5 mg, 0.041 mmol). The mixture was warmed to –30 °C over a period of 1 h, and Tf_2NPh (15 mg, 0.041 mmol) was added. The mixture was stirred for 24 h, poured into sat. NH_4Cl (10 mL) and diluted with Et_2O (10 mL). The organic layer was washed with H_2O (10 mL), dried

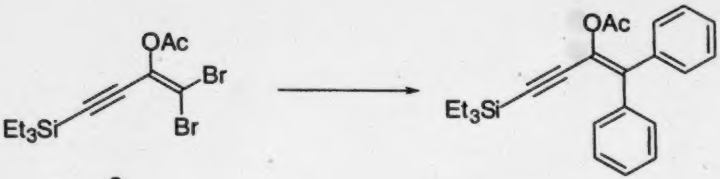
(Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et_2O 10:1) to give **17** (6.4 mg, 0.010 mmol, 37% based on recovered starting material) as a bright yellow oil and recovered starting material (6.5 mg, 0.012 mmol, 31%). R_f = 0.3 (hexanes/Et_2O 10:1). IR (CH_2Cl_2, cast) 3058, 2957, 2912, 2876, 2193, 2134, 1585, 1506, 1457, 1426, 1374, 1333 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.4-8.5 (m, 2H), 7.8-8.0 (m, 6H), 7.48-7.68 (m, 6H), 1.03 (t, J = 8.0 Hz, 9H), 0.74 (q, J = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 137.9, 133.6, 133.58, 133.56, 133.4, 132.1, 131.8, 130.9, 130.7, 128.86, 128.82, 127.8, 127.7, 127.2, 127.1, 126.2, 125.7, 125.6, 119.5, 119.4, 118.8 (q, J = 319 Hz, CF_3), 112.8, 109.3, 101.0, 96.9, 96.6, 87.8, 87.0, 7.5, 4.3 (1 coincident signal); EIMS *m/z* 614 (M^+, 14), 481 ($[M - SO_2CF_3]^+$, 100); HRMS calcd. for $C_{35}H_{29}O_3SiF_3S$ (M^+) 614.1558, found 614.1563. Anal. calcd. for $C_{35}H_{29}O_3SiF_3S$: C, 68.40; H, 4.72. Found: C; 67.86, H; 4.59.



14 **18**

4-Ferrocenylethynyl-6-ferrocenyl-1-triethylsilyl-3-trifluoromethanesulfoxy-hex-3-en-1,5-diyne (18)

Compound **14** (105 mg, 0.163 mmol) was dissolved in THF (7 mL) and cooled to –78 °C. To this was added MeLi (0.21 mL, 0.33 mmol, 1.6 M in Et_2O). The mixture was stirred at –78 °C for 1 h, and Tf_2O (92 mg, 0.33 mmol) was added. The mixture was stirred for 20 min, poured into sat. NH_4Cl (10 mL) and diluted with Et_2O (10 mL). The organic layer was washed with H_2O (2 x 10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et_2O 15:1) to yield **18** (86 mg, 0.12 mmol, 72%) as a dark red oil. $R_f = 0.2$ (hexane/Et_2O 18:1). IR (CH_2Cl_2, cast) 3096, 2956, 2874, 2196, 2135, 1457, 1425, 1324, 1248 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.57 (t, $J = 1.8$ Hz, 2H), 4.50 (t, $J = 1.8$ Hz, 2H), 4.31 (t, $J = 1.8$ Hz, 2H), 4.29 (t, $J = 1.8$ Hz, 2H), 4.28 (s, 5H), 4.25 (s, 5H), 1.0 (t, $J = 8.1$ Hz, 9H), 0.71 (q, $J = 8.1$ Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 136.3, 118.4 (q, $J = 321$ Hz, CF_3), 110.1, 109.9, 103.4, 98.4, 97.0, 79.6, 79.2, 72.0, 71.9, 70.4, 70.3, 69.9, 69.7, 63.3, 62.9, 7.5, 4.1; EIMS *m/z* 730 (M^+, 10), 597 ($[M - SO_2CF_3]^+$, 17); HRMS calcd. for $C_{35}H_{33}F_3FeO_3SSi$ (M^+) 730.0571, found 730.0573.

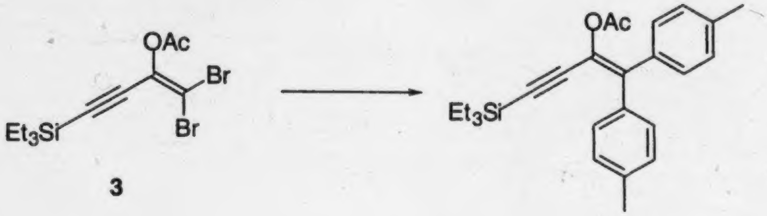


3 **19**

2-Acetoxy-1,1-diphenyl-4-triethylsilyl-but-1-en-3-yne (19)

To a dry, degassed solution of compound **3** (100 mg, 0.262 mmol) and phenyl boronic acid (70.2 mg, 0.576 mmol) in toluene (7 mL) was added K_2CO_3 (80 mg, 0.58 mmol) and $Pd(PPh_3)_4$ (15.1 mg, 0.0131 mmol). The mixture was refluxed for 12 h, filtered through celite and diluted with Et_2O (10 mL). The organic layer was washed with sat. NH_4Cl (2 x 10 mL), H_2O (10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et_2O 10:1) to yield **19** (62 mg, 0.17 mmol, 63%) as a light yellow solid, Mp 72-73 °C. $R_f = 0.4$ (hexane/Et_2O 10:1). IR (CH_2Cl_2, cast) 3056, 2955, 2911, 2874, 2144, 1769, 1600, 1494, 1457, 1443, 1414, 1367, 1214 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.43-7.50 (m, 2H), 7.22-7.32 (m, 6H), 7.15-7.20 (m, 2H), 1.97 (s, 3H), 0.89 (t, $J = 7.8$ Hz, 9H), 0.54 (q, $J = 7.8$ Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$, APT) δ 168.3, 140.1, 138.1, 137.8, 130.4, 129.4, 128.2, 128.0, 127.9, 127.8, 126.8, 100.3, 98.3, 20.7, 7.4, 4.1; EIMS *m/z*

376 (M^+, 17), 334 ($[M - C_2H_2O]^+$, 100); HRMS calcd. for $C_{24}H_{28}O_2Si$ (M^+) 376.1859, found 376.1862.

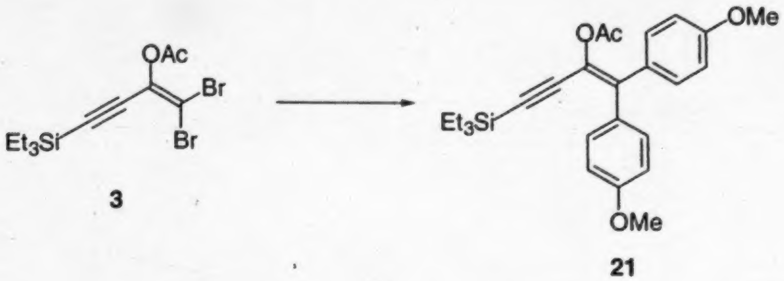


3

20

2-Acetoxy-1,1-di-p-tolyl-4-triethylsilyl-but-1-en-3-yne (20)

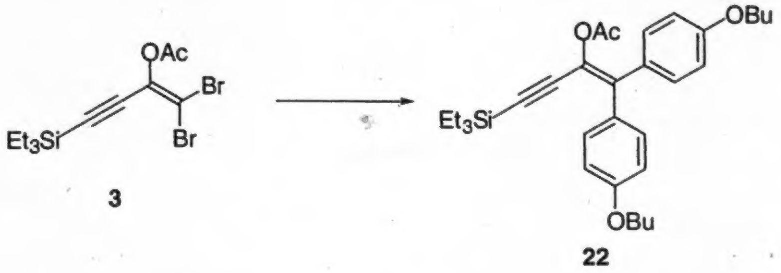
To a dry, degassed solution of compound **3** (200 mg, 0.524 mmol) and *p*-tolylboronic acid (157 mg, 1.15 mmol) in toluene (7 mL) was added K_2CO_3 (159 mg, 1.15 mmol) and $Pd(PPh_3)_4$ (30.3 mg, 0.0262 mmol). The mixture was refluxed for 12 h, filtered through celite and diluted with Et_2O (10 mL). The organic layer was washed with sat. NH_4Cl (2 x 10 mL), H_2O (10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et_2O 10:1) to yield **20** (146 mg, 0.36 mmol, 69%) as a yellow oil. R_f = 0.4 (hexane/ Et_2O 10.1). IR (CH_2Cl_2, cast) 3025, 2955, 2913, 2874, 2147, 1769, 1610, 1511, 1457, 1413, 1367, 1213 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.0 Hz, 2H), 7.05-7.10 (m, 6H), 2.32 (br s, 2 x CH_3), 0.90 (t, J = 8.0 Hz, 9H), 0.55 (q, J = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$, APT) δ 169.2, 140.0, 137.9, 137.6, 135.3, 135.0, 130.2, 129.2, 128.6, 128.3, 126.1, 100.6, 97.9, 21.4, 21.3, 20.9, 7.4, 4.3; EIMS *m/z* 404 (M$^+$, 24), 362 ([M – C$_2$H$_2$O]$^+$, 100); HRMS calcd. for $C_{26}H_{32}O_2Si$ (M$^+$) 404.2171, found 404.2171. Anal. calcd. for $C_{26}H_{32}O_2Si$: C, 76.22; H, 7.99. Found: C, 76.66; H, 7.94.



21

2-Acetoxy-1,1-bis-(4-methoxyphenyl)-4-triethylsilyl-but-1-en-3-yne (21)

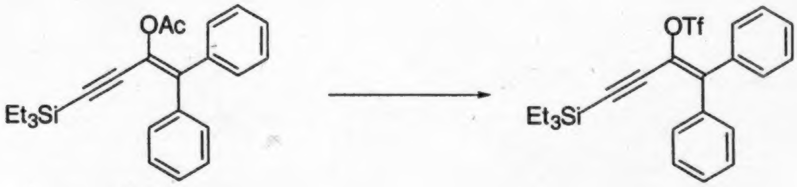
To a dry, degassed solution of compound **3** (200 mg, 0.524 mmol) and *p*-methoxyphenyl boronic acid (176 mg, 1.16 mmol) in toluene (7 mL) was added K$_2$CO$_3$ (160 mg, 1.16 mmol) and Pd(PPh$_3$)$_4$ (30.2 mg, 0.0262 mmol). The mixture was refluxed for 12 h, filtered through celite and diluted with Et$_2$O (10 mL). The organic layer was washed with sat. NH$_4$Cl (2 x 10 mL), H$_2$O (10 mL), brine (10 mL), dried (Na$_2$SO$_4$), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et$_2$O 5:1) to yield **21** (115 mg, 0.263 mmol, 50%) as a light yellow oil. R$_f$ = 0.2 (hexane/Et$_2$O 5:1). IR (CH$_2$Cl$_2$, cast) 3000, 2955, 2910, 2874, 2836, 2143, 1765, 1606, 1572, 1510, 1463, 1441, 1414, 1367 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 9.0 Hz, 2H), 6.78 (d, *J* = 9.0 Hz, 2H), 3.78 (s, 3H), 3.77 (s, 3H), 1.99 (s, 3H); 0.90 (t, *J* = 8.9 Hz, 9H), 0.54 (q, *J* = 8.9 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.3, 159.4, 159.0, 139.3, 131.7, 130.7, 130.5, 130.3, 125.4, 113.3, 113.0, 100.8, 97.5, 55.3, 55.2, 20.9, 7.4, 4.2; EIMS *m/z* 436 (M^+, 26), 394 ($[M - C_2H_2O]^+$, 100); HRMS calcd. for $C_{26}H_{32}O_4Si$ (M^+) 436.2070, found 436.2066.



2-Acetoxy-1,1-bis-(4-butoxyphenyl)-4-triethylsilyl-but-1-en-3-yne (22)

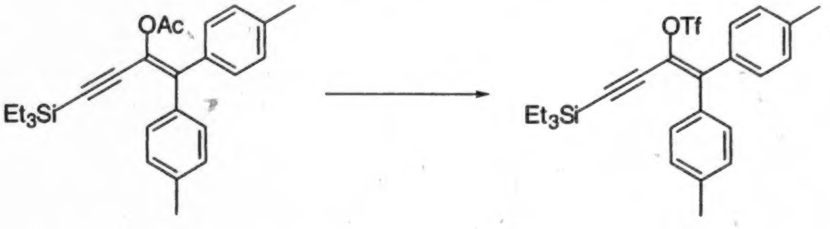
To a dry, degassed solution of compound **3** (200 mg, 0.524 mmol) and *p*-butoxyphenyl boronic acid (398 mg, 2.09 mmol) in toluene (7 mL) was added K_2CO_3 (362 mg, 2.62 mmol) and $Pd(PPh_3)_4$ (30.3 mg, 0.0262 mmol). The mixture was refluxed for 12 h, filtered through celite and diluted with Et_2O (10 mL). The organic layer was washed with sat. NH_4Cl (2 x 10 mL), H_2O (10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et_2O 15:1) to yield **22** (239 mg, 0.460

mmol, 85%) as a light yellow oil. R_f = 0.2 (hexane/Et_2O 15:1). IR (CH_2Cl_2, cast) 3039, 2957, 2934, 2873, 2144, 1768, 1606, 1570, 1467, 1414, 1367, 1304 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 3.91-3.98 (m, 4H), 2.00 (s, 3H), 1.70-1.79 (m, 4H), 1.43-1.53 (m, 4H), 0.96 (t, *J* = 7.6 Hz, 6H), 0.91 (t, *J* = 8.0 Hz, 9H), 0.56 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 159.1, 158.8, 139.6, 131.8, 130.8, 130.4, 130.2, 125.3, 113.8, 113.6, 100.9, 97.5, 67.6, 67.5, 31.3, 31.2, 20.8, 19.2, 19.1, 13.8, 13.7, 7.3, 4.1; EIMS *m/z* 520 (M^+, 34), 478 ($[M - C_2H_2O]^+$, 100); HRMS calcd. for $C_{32}H_{44}O_4Si$ (M^+) 520.3009, found 520.3000. EA attempted but unsuccessful.



19 **23**

1,1-diphenyl-4-triethylsilyl-2-trifluoromethanesulfoxy-but-1-en-3-yne (23) Compound **19** (52 mg, 0.138 mmol) was dissolved in THF (3 mL) and cooled to –20 °C. To this was added MeLi (0.17 mL, 0.27 mmol, 1.6 M in Et_2O). The mixture was stirred at –20 °C for 1 h, and Tf_2O (78.2 mg, 0.277 mmol) was added. The mixture was stirred for 20 min, poured into sat. NH_4Cl (10 mL) and diluted with Et_2O (10 mL). The organic layer was washed with H_2O (2 x 10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et_2O 10:1) to yield **23** (43 mg, 0.092 mmol, 67%) as a light yellow oil. Spectral data consistent with those previously reported (Zhao, Tykwinski, unpublished results). R_f = 0.5 (hexane/Et_2O 10:1). ^1H NMR (300 MHz, $CDCl_3$) δ 7.42-7.47 (m, 2H), 7.23-7.37 (m, 8H) 0.91 (t, *J* = 7.8 Hz, 9H), 0.57 (q, *J* = 7.8 Hz, 6H), ^{13}C (100 MHz, $CDCl_3$, APT) δ 143.9, 136.9, 136.1, 130.4, 130.1, 139.6, 129.1, 128.4, 128.1, 126.4, 118.2 (q, *J* = 319 Hz, CF_3), 103.1, 97.4, 7.21, 3.93.

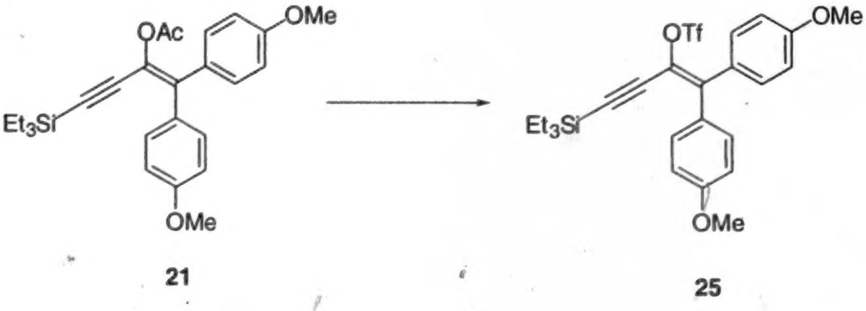


20 **24**

4-Triethylsilyl-2-trifluoromethanesulfoxy-1,1-di-p-tolyl-but-1-en-3-yne (24)

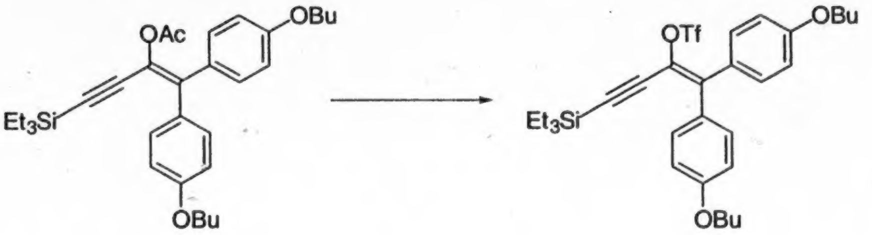
Compound **20** (100 mg, 0.248 mmol) was dissolved in THF (5 mL) and cooled to –78 °C. To this was added MeLi (0.31 mL, 0.50 mmol, 1.6 M in Et_2O). The mixture was stirred at –78 °C for 1 h, and Tf_2O (140 mg, 0.495 mmol) was added.

The mixture was stirred for 20 min, poured into sat. NH_4Cl (10 mL) and diluted with Et_2O (10 mL). The organic layer was washed with H_2O (2 x 10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et_2O 15:1) to yield **24** (77 mg, 0.16 mmol, 63%) as a brown solid, Mp 50-52 °C. $R_f = 0.7$ (hexane/Et_2O 10:1). IR (CH_2Cl_2, cast) 3029, 2957, 2914, 2877, 2147, 1610, 1511, 1458, 1423, 1379, 1246, 1209, cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, $J = 8.0$ Hz, 2H) 7.08-7.15 (M, 6H), 2.34 (br s, 2 x CH_3), 0.91 (t, $J = 7.6$ Hz, 9H), 0.57 (q, J = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, APT) δ 143.9, 139.3, 139.1, 134.0, 133.2, 130.8, 130.3, 129.9, 128.6, 125.8, 118.2 (q, $J = 318$ Hz, CF_3), 102.5, 97.7, 21.5, 21.4, 7.3, 4.1; EIMS *m/z* 494 (M^+, 18), 361 ($[M - SO_2CF_3]^+$, 100); HRMS calcd. for $C_{25}H_{29}O_3SSiF_3$ (M^+) 494.1559, found 494.1562. Anal calcd. for $C_{25}H_{29}O_3SSiF_3$: C, 60.73; H, 5.87. Found: C, 60.82; H, 6.34.



1,1-bis-(4-methoxyphenyl)-4-triethylsilyl-2-trifluoromethanesulfoxy-but-1-en-3-yne (25)

Compound **21** (59 mg, 0.135 mmol) was dissolved in THF (3 mL) and cooled to –20 °C. To this was added MeLi (0.17 mL, 0.27 mmol, 1.6 M in Et_2O). The mixture was stirred at –20 °C for 1 h, and Tf_2O (76.5 mg, 0.271 mmol) was added. The mixture was stirred for 20 min, poured into sat. NH_4Cl (10 mL) and diluted with Et_2O (10 mL). The organic layer was washed with H_2O (2 x 10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et_2O 5:1) to yield **25** (46 mg, 0.087 mmol, 65%) as a colorless oil. $R_f = 0.6$ (hexane/Et_2O 5:1). IR (CH_2Cl_2, cast) 2957, 2912, 2876, 2839, 2144, 1606, 1574, 1511, 1463, 1442, 1420 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, $J = 9.0$ Hz, 2H), 7.17 (d, $J = 9.0$ Hz, 2H), 6.86 (d, $J = 9.0$ Hz, 2H), 6.82 (d, $J = 9.0$ Hz, 2H), 3.8 (s, 3H), 3.79 (s, 3H), 0.91 (t, $J = 7.8$ Hz, 9H), 0.57 (q, $J = 7.8$ Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$, APT) δ 160.5, 130.2, 143.1, 132.1, 131.8, 129.3, 128.5, 125.2, 118.3 (q, $J = 321$ Hz, CF_3), 113.7, 113.4, 102.2, 98.1, 55.4, 55.3, 7.2, 4.0; EIMS *m/z* 526 (M^+, 19), 393 ($[M - SO_2CF_3]^+$, 100); HRMS calcd. for $C_{25}H_{29}O_3SSiF_3$ (M^+) 526.1456, found 526.1457.

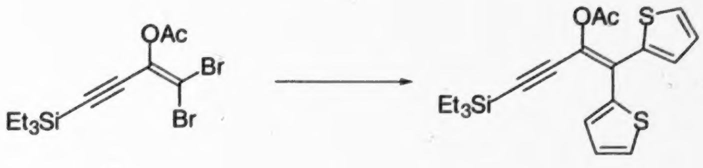


22 26

1,1-bis-(4-butoxyphenyl)-4-triethylsilyl-2-trifluoromethanesulfoxy-but-1-en-3-yne (26)

Compound **22** (200 mg, 0.385 mmol) was dissolved in THF (5 mL) and cooled to –78 °C. To this was added MeLi (0.48 mL, 0.77 mmol, 1.6 M in Et_2O). The mixture was stirred at –78 °C for 1 h, and Tf_2O (217 mg, 0.769 mmol) was added. The mixture was stirred for 20 min, poured into sat. NH_4Cl (10 mL) and diluted with Et_2O (10 mL). The organic layer was washed with H_2O (2 x 10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et_2O 10:1) to yield **26** (164 mg, 0.269 mmol, 70%) as a yellow semi-solid. R_f = 0.5 (hexane/Et_2O 10:1). IR (CH_2Cl_2, cast) 3041, 2958, 2875, 2144, 1606, 1572, 1511, 1468, 1421, 1305 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 9.2 Hz, 2H), 7.16 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 9.2 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 3.93-3.98 (m, 4H), 1.7-1.8 (m, 4H), 1.42-

1.54 (m, 4H), 0.97 (t, $J = 7.2$ Hz, 6H), 0.92 (t, $J = 8.0$ Hz, 9H), 0.57 (q, $J = 8.0$ Hz, 6H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 160.6, 160.3, 144.2, 132.4, 132.1, 129.2, 128.6, 125.4, 118.6 (q, $J = 319$ Hz, CF_3), 114.5, 114.3, 102.0, 98.2, 68.2, 68.1, 31.7, 31.6, 19.6, 19.5, 14.0, 13.9, 7.3, 4.3; EIMS *m/z* 610 (M^+, 34), 477 ($[M - SO_2CF_3]^+$, 100); HRMS calcd. for $C_{31}H_{41}O_5F_3SSi$ (M^+) 610.2396, found 610.2394.

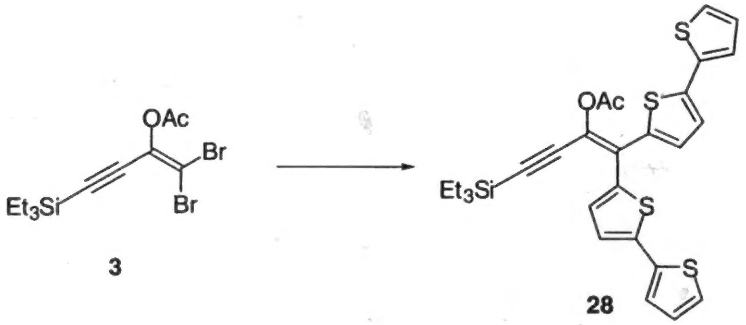


3

27

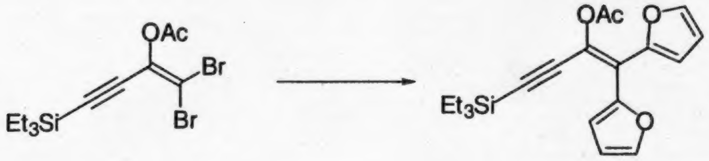
2-Acetoxy-1,1-(di-2-thiophenyl)-4-triethylsilyl-but-1-en-3-yne (27)

To a degassed solution of compound **3** (50 mg, 0.131 mmol) and 2-tributylstannylthiophene (150 mg, 0.393 mmol) in DMF (5 mL) was added $Pd(PPh_3)_4$ (7.5 mg, 0.007 mmol). The mixture was heated to 120 °C for 2 h, then cooled to rt and poured into H_2O (10 mL) and diluted with Et_2O (10 mL). The organic layer was washed with brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et_2O 25:1) to yield **27** (34 mg, 0.088 mmol, 66%) as a light green oil. R_f = 0.3 (hexanes/Et_2O 20:1). IR (CH_2Cl_2, cast) 3105, 2955, 2910, 2874, 2141, 1774, 1457, 1420, 1367, 1349 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (t, *J* = 5.5 Hz, 1H), 7.36 (t, *J* = 5.5 Hz, 1H), 7.24 (dd, *J* = 1.0, 4.0 Hz, 1H), 7.01 (dd, *J* = 4.0, 5.5 Hz, 1H), 6.96 (dd, *J* = 4.0, 5.5 Hz, 1H), 6.92 (dd, *J* = 1.0, 4.0 Hz, 1H), 2.24 (s, 3H), 0.89 (t, *J* = 8.0 Hz, 9H), 0.54 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, APT) δ 167.5, 138.5, 138.0, 129.9, 129.8, 127.9, 126.8, 126.7, 126.6, 126.4, 126.3, 102.4, 99.6, 21.3, 7.4, 4.1; EIMS *m/z* 388 (M^+, 3); HRMS calcd. for $C_{20}H_{24}SiS_2O_2$ (M^+) 388.0986, found 388.0983.



2-Acetoxy-1,1-[bis-(2,2')-bithiophenyl]-4-triethylsilyl-but-1-en-3-yne (28)

To a degassed solution of compound **3** (60 mg, 0.157 mmol) and 2-tributylstannyl-2,2'-bithiophene (180 mg, 0.396 mmol) in DMF (5 mL) was added $Pd(PPh_3)_4$ (8.0 mg, 0.0069 mmol). The mixture was heated to 120 °C for 2 h, then cooled to rt and poured into H_2O (10 mL) and diluted with Et_2O (10 mL). The organic layer was washed with brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et_2O 5:1) to yield **28** (43 mg, 0.078 mmol, 50%) as a light green oil. R_f = 0.4 (hexane/ Et_2O 5:1). IR (CH_2Cl_2, cast) 3106, 3070, 2954, 2909, 2873, 2137, 1774, 1456, 1444, 1423, 1367, 1308 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.90-7.26 (m, 10H), 2.26 (s, 3H), 0.92 (t, *J* = 8.0 Hz, 9H), 0.57 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, APT) δ 167.9, 140.1, 139.2, 137.4, 137.1, 136.9, 131.3, 131.1, 128.2, 128.1, 126.9, 126.5, 125.3, 124.9, 124.3, 124.1, 123.5, 123.4, 104.1, 100.1, 21.6, 7.6, 4.4, (1 coincident signal); EIMS *m/z* 552 (M^+, 29), 510 ($[M - C_2H_2O]^+$, 100); HRMS calcd. for $C_{28}H_{28}O_2SiS_4$ (M^+) 552.0741, found 552.0738.

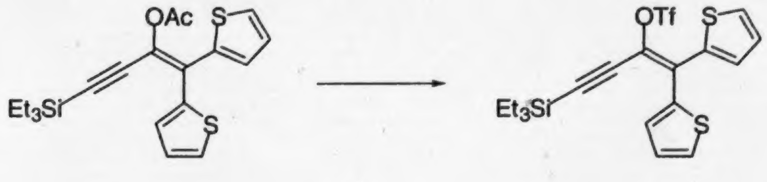


3

29

2-Acetoxy-1,1-(di-2-furanyl)-4-triethylsilyl-but-1-en-3-yne (29)

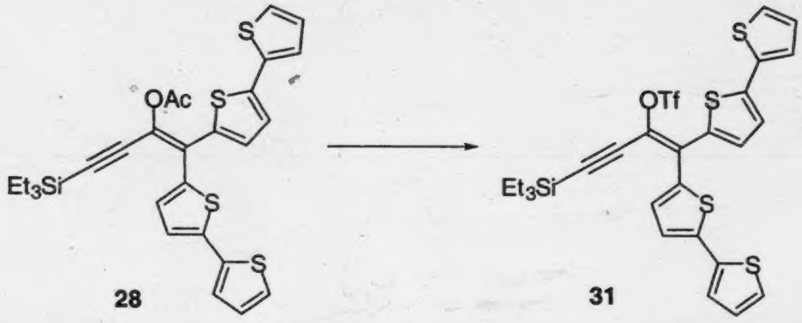
To a degassed solution of compound **3** (100 mg, 0.262 mmol) and 2-tributylstannylfuran (280 mg, 0.785 mmol) in DMF (5 mL) was added $Pd(PPh_3)_4$ (15.0 mg, 0.0131 mmol). The mixture was heated to 120 °C for 4 h, then cooled to rt and poured into H_2O (10 mL) and diluted with Et_2O (10 mL). The organic layer was washed with brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et_2O gradient elution 20:1-5:1) to yield **29** (53 mg, 0.15 mmol, 57%) as a light red oil. R_f = 0.3 (hexane/Et_2O 10:1). IR (CH_2Cl_2, cast) 3120, 2956, 2911, 2875, 2139, 1772, 1546, 1466, 1414, 1367, 1313 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40-7.44 (m, 2H), 6.80 (d, *J* = 3.3 Hz, 1H), 6.40-6.50 (m, 3H), 2.19 (s, 3H), 0.95 (t, *J* = 7.8 Hz, 9H), 0.60 (q, *J* = 7.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, APT) δ 168.3, 148.3, 147.8, 143.3, 142.7, 126.3, 119.7, 113.4, 113.3, 111.4, 111.0, 101.8, 100.2, 20.9, 7.4, 4.1; EIMS *m/z* 356 (M^+, 15), 314 ($[M - C_2H_2O]^+$, 100); HRMS calcd. for $C_{20}H_{24}O_4Si$ (M^+) 356.1443, found 356.1441.



27 **30**

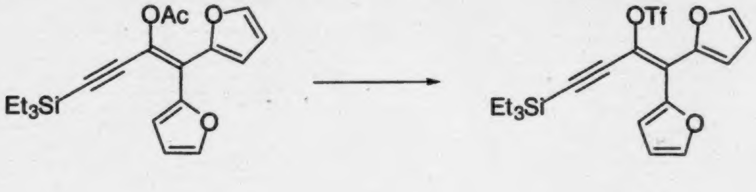
1,1-(di-2-thiophenyl)-4-triethylsilyl-2-trifluoromethanesulfoxy-but-1-en-3-yne (30)

Compound **27** (35 mg, 0.090 mmol) was dissolved in THF (3 mL) and cooled to –78 °C. To this was added MeLi (0.11 mL, 0.18 mmol, 1.6 M in Et_2O). The mixture was stirred at –78 °C for 1 h, and Tf_2O (51 mg, 0.016 mmol) was added. The mixture was stirred for 20 min, poured into sat. NH_4Cl (10 mL) and diluted with Et_2O (10 mL). The organic layer was washed with H_2O (2 x 10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et_2O 15:1) to yield **30** (37 mg, 0.077 mmol, 85%) as a light green oil. $R_f = 0.6$ (hexane/ Et_2O 10:1). IR (CH_2Cl_2, cast) 3109, 3077, 2958, 2913, 2877, 2142, 1579, 1523, 1504, 1457, 1424, 1380, 1365, 1348 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 1.2, 5.1 Hz, 1H), 7.43 (dd, *J* = 1.2, 5.1 Hz, 1H), 7.33 (dd, *J* = 1.2, 5.1 Hz, 1H), 7.19 (dd, *J* = 1.2, 5.1 Hz, 1H), 7.06 (dd, *J* = 3.6, 5.1 Hz, 1H), 7.02 (dd, *J* = 3.6, 5.1 Hz, 1H), 0.96 (t, *J* = 7.8 Hz, 9H), 0.63 (q, *J* = 7.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.6, 136.4, 131.7, 131.3, 130.3, 129.3, 128.7, 127.1, 126.8, 125.2, 118.2 (q, *J* = 320 Hz, *C*F_3), 108.2, 97.1, 7.2, 3.8; EIMS *m/z* 478 (M^+, 10), 345 ($[M - SO_2CF_3]^+$, 100); HRMS calcd. for $C_{19}H_{21}S_3O_3F_3Si$ (M^+) 478.0374, found 478.0382.



1,1-[bis-(2,2')-bithiophenyl]-4-triethylsilyl-2-trifluoromethanesulfoxy-but-1-en-3-yne (31)

Compound **28** (35 mg, 0.063 mmol) was dissolved in THF (3 mL) and cooled to –78 °C. To this was added MeLi (0.079 mL, 0.13 mmol, 1.6 M in Et_2O). The mixture was stirred at –78 °C for 1 h, and Tf_2O (36 mg, 0.13 mmol) was added. The mixture was stirred for 20 min, poured into sat. NH_4Cl (10 mL) and diluted with Et_2O (10 mL). The organic layer was washed with H_2O (2 x 10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et_2O 15:1) to yield **31** (24 mg, 0.037 mmol, 60%) as a dark green oil. R_f = 0.6 (hexane/ Et_2O 10:1). IR (CH_2Cl_2, cast) 3072, 2956, 2911, 2875, 2138, 1441, 1423, 1308 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.23-7.27 (m, 3H), 7.20 (dd, *J* = 0.9, 3.6 Hz, 1H), 7.18 (dd, *J* = 0.9, 3.6 Hz, 1H), 7.14 (s, br, 2H), 7.09 (dd, *J* = 0.9, 3.6 Hz, 1H), 7.02 (t, *J* = 3.6 Hz, 1H), 7.00 (t, *J* = 3.9 Hz, 1H), 0.98 (t, *J* = 7.8 Hz, 9H), 0.66 (q, *J* = 7.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.4, 140.7, 136.7, 136.4, 135.6, 134.4, 133.0, 132.2, 129.7, 128.07, 128.05, 125.4, 125.0, 124.6, 124.4, 123.6, 123.2, 118.3 (q, *J* = 321 Hz, CF_3), 109.5, 97.3, 7.3, 3.9 (1 coincident signal); ESI HRMS calcd. for $C_{27}H_{26}O_3F_3SiS_5$ $(M + H)^+$ 643.0206, found 643.0206, solvent: MeOH/toluene 4:1.

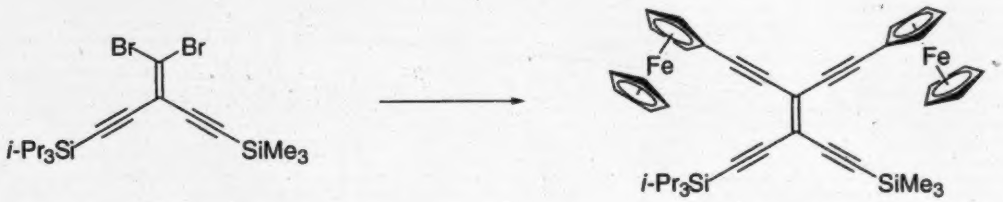


29 **32**

1,1-(Di-2-furanyl)-4-triethylsilyl-2-trifluoromethanesulfoxy-but-1-en-3-yne (32)

Compound **29** (43 mg, 0.121 mmol) was dissolved in THF (5 mL) and cooled to –78 °C. To this was added MeLi (0.15 mL, 0.24 mmol, 1.6 M in Et_2O). The mixture was stirred at –78 °C for 1 h, and Tf_2O (68 mg, 0.24 mmol) was added. The mixture was stirred for 20 min, poured into sat. NH_4Cl (10 mL) and diluted with Et_2O (10 mL). The organic layer was washed with H_2O (2 x 10 mL), brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et_2O 10:1) to yield **32** (31 mg, 0.069

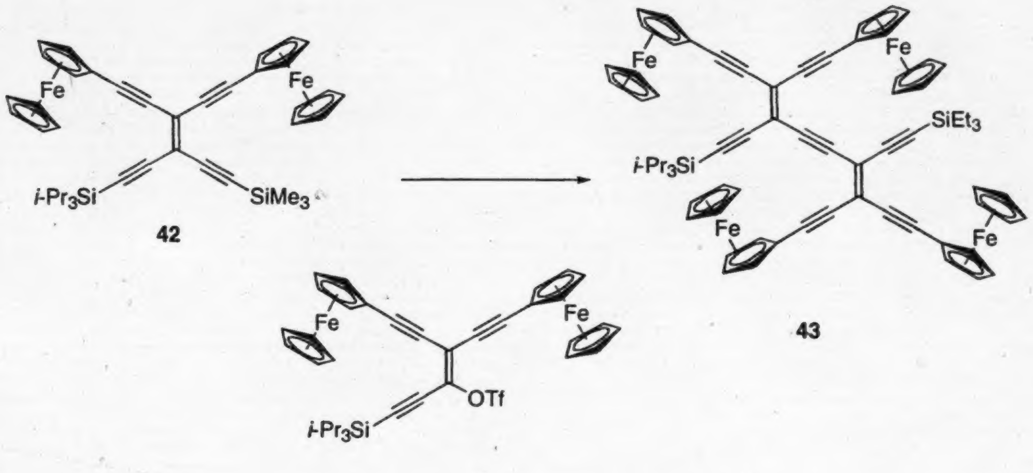
mmol, 57%) as a light yellow oil. R_f = 0.4 (hexane/Et_2O 10:1). IR (CH_2Cl_2, cast) 3154, 2958, 2914, 2877, 2141, 1568, 1467, 1425, 1380, 1316 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.54-7.58 (m, 1H), 7.46-7.52 (m, 1H), 6.82-6.88 (m, 1H), 6.62-6.68 (m, 1H), 6.46-6.54 (m, 2H), 0.97 (t, *J* = 8.1 Hz, 9H), 0.63 (q, *J* = 8.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 144.6, 143.9, 124.8, 122.1, 118.3 (q, *J* = 319 Hz, CF_3), 116.1, 115.3, 111.9, 111.5, 106.7, 97.5, 7.2, 3.9 (1 coincident signal); EIMS *m/z* 446 (M^+, 9), 313 ($[M - SO_2CF_3]^+$, 100); HRMS calcd. for $C_{19}H_{21}O_5F_3SiS$ (M^+) 446.0831, found 446.0834.



41 **42**

1-Ferrocenyl-3-ferrocenylethynyl-4-trimethylsilylethynyl-6-triisopropylsilyl-hex-3-en-1,5-diyne (42)

To a degassed solution of **33** (100 mg, 0.25 mmol) and ethynylferrocene (155 mg, 0.74 mmol) in Et_3N (10 mL) was added $PdCl_2(PPh_3)_2$ (8.6 mg, 0.012 mmol) and CuI (20 mg, 0.011 mmol). The mixture was stirred at 40 °C for 48 h, cooled to rt and poured into sat. NH_4Cl (20 mL). The mixture was diluted with Et_2O (30 mL) and the organic layer was washed with brine (20 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et_2O 15:1) to yield **42** (50 mg, 0.69 mmol, 28%) as an orange oil. R_f = 0.5 (hexane/Et_2O 20:1). IR (CH_2Cl_2, cast) 3095, 2941, 2863, 2188, 2138, 1732, 1694, 1651, 1616, 1575, 1504, 1462, 1411, 1383 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.51 (t, J = 1.5 Hz, 2H), 4.49 (t, J = 1.5 Hz, 2H), 4.28 (t, J = 1.5 Hz, 2H), 4.27 (t, J = 1.5 Hz, 2H), 4.25 (s, 5H), 4.22 (s, 5H), 1.14 (s, 21H), 0.27 (s, 9H); ^{13}C NMR (125 MHz, CD_2Cl_2, APT) δ 119.6, 113.2, 104.6, 103.8, 103.0, 101.3, 99.9, 99.5, 84.5, 84.4, 72.2, 70.7, 70.6, 70.2, 70.1, 64.2, 18.9, 11.7, 0.03 (2 coincident signals); EIMS *m/z* 720 (M^+, 100); HRMS calcd. for $C_{42}H_{48}Fe_2Si_2$ (M^+) 720.1993, found 720.2005.



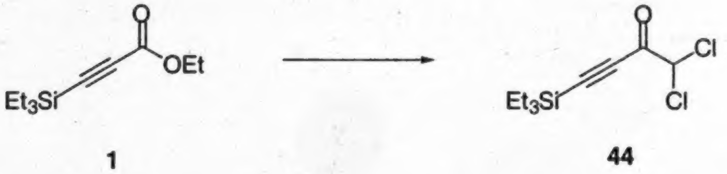
42

43

18

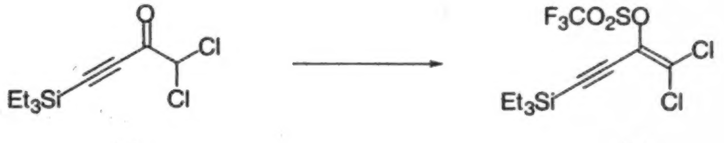
1,10-Ferrocenyl-2,8-ferrocenylethynyl-7-triethylsilylethynyl-4-triisopropylsilylethynyl-deca-3,7-dien-1,5,9-triyne (43)

Compound **33** (21 mg, 0.029 mmol) was desilylated using K_2CO_3 (2 mg) in wet MeOH/THF (3 mL, 1:1). After 30 min, the mixture was diluted with Et_2O (10 mL). The organic layer was washed with H_2O (10 mL), brine (10 mL), dried (Na_2SO_4), filtered, evaporated to 1 mL. The solution was added to **18** (21 mg, 0.029 mmol) and dissolved in Et_3N (5 mL). The solution was degassed for 40 min, then $Pd(PPh_3)_4$ (1.7 mg, 0.0015 mmol) and CuI (3mg, 0.02 mmol) was added. The mixture was stirred at rt for 2 h, poured into sat. NH_4Cl (10 mL) and diluted with Et_2O (20 mL). The organic layer was washed with brine (20 mL), dried (Na_2SO_4) and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et_2O 10:1) to yield **43** (24 mg, 0.020 mmol, 67%) as a purple solid, Mp 78-80 °C, R_f = 0.4 (hexane/Et_2O 10:1). IR (CH_2Cl_2, cast) 3095, 2954, 2864, 2184, 2135, 1732, 1651, 1504, 1462, 1411, 1383, 1306 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.54-4.57 (m, 4H), 4.49-4.52 (m, 4H), 4.20-4.30 (m, 28H), 1.14 (s, 21H), 1.06 (t, J = 6.4 Hz, 9H), 0.70 (q, J = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, APT) δ 125.5, 120.1, 120.0, 115.3, 113.5, 113.3, 103.7, 103.1, 101.8, 101.0, 100.3, 100.1, 99.7, 95.6, 95.2, 84.6, 84.5, 84.3, 72.1, 72.0, 71.9, 71.8, 70.6, 70.5, 70.3, 70.2, 69.7, 69.68, 69.64, 69.5, 68.1, 64.1, 64.1, 18.8, 11.3, 7.7, 4.4 (1 carbon not observed); ESI MS 1228 (M^+,100), solvent: nitromethane.



1,1-Dichloro-4-triethylsilyl-but-2-one-3-yne (44)

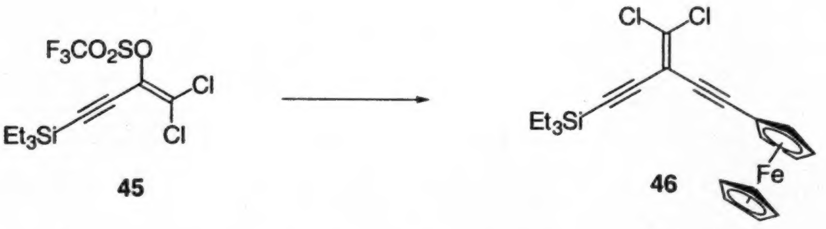
To a stirred solution of dichloromethane (401 mg, 0.302 mL, 4.72 mmol) and compound **1** (500 mg, 2.32 mmol) in Et_2O (10 mL) at –78 °C was added a solution of LDA (4.72 mmol) in Et_2O (10 mL) over a period of 5 min. The mixture was stirred for 20 min at –78 °C and then hydrolyzed with H_2SO_4 (0.25 mL) in Et_2O (2 mL). The mixture was stirred for 30 min at –78 °C and filtered through celite. The solution was evaporated and passed through a plug of silica gel (hexane/Et_2O 40:1) to yield **44** (378 mg, 1.51 mmol, 65%) as a pale yellow oil. R_f = 0.8 (hexane/Et_2O 30:1). IR (CH_2Cl_2, cast) 2959, 2937, 2913, 2877, 2156, 1688, 1458, 1414, 1381 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.88 (s, 1H), 1.03 (t, *J* = 6.0 Hz, 9H), 0.71 (q, *J* = 6.0 Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 173.2, 105.4, 98.0, 69.9, 7.3, 3.7; EIMS *m/z* 250 (M^+, 4), 167 ($[M - CHCl_2]^+$, 100); HRMS calcd. for $C_{10}H_{16}OSi^{35}Cl_2$ 250.0347, found 250.0359.



44 **45**

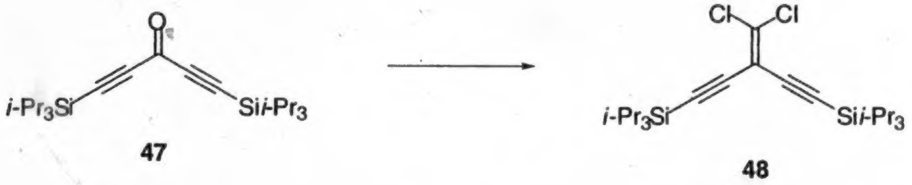
1,1-Dichloro-4-triethylsilyl-2-trifluoromethanesulfoxy-but-1-en-3-yne (45)

To a mixture of **36** (211 mg, 0.839 mmol) and HMPA (225 mg, 1.26 mmol) in THF (5 mL) at –78 °C was added LiHMDS (1.09 mmol) in THF (5 mL). The mixture was stirred at –78 °C for 30 min and *N*-phenyltriflimide (360 mg, 1.01 mmol) in THF (6 mL) was added. The solution was allowed to warm to rt over 3 h. Sat. NH_4Cl (10 mL) was added and the mixture was extracted with Et_2O (2 x 30 mL), the organic layer washed with brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexanes) to yield **45** (200 mg, 0.525 mmol, 63%) as a colorless oil. R_f = 0.7 (hexanes). IR (CH_2Cl_2, cast) 2960, 2915, 2879, 1457, 1436, 1381 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.00 (t, *J* = 5.7 Hz, 9H), 0.67 (q, *J* = 5.7 Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$, APT) δ 129.6, 128.2, 118.2 (q, *J* = 320 Hz, *C*F_3), 110.2, 92.6, 7.2, 3.8; EIMS *m/z* 381 (M^+, 29); HRMS calcd. for $C_{11}H_{15}O_3Si^{35}Cl_2SF_3$ (M^+) 381.9840, found 381.9835.



3-Dichloromethylidene-1-ferrocenyl-5-triethylsilyl-penta-1,4-diyne (46)

Compound **45** (100 mg, 0.26 mmol) and ethynylferrocene (110 mg, 0.32 mmol) were dissolved in Et_3N (10 ml) and the resulting mixture was degassed for 30 min. $PdCl_2(PPh_3)_2$ (9.2 mg, 0.013 mmol) and CuI (18 mg, 0.095 mmol) were added and the mixture stirred at 50 °C for 2 h. The mixture was poured into sat. NH_4Cl (20 mL), extracted with Et_2O (30 mL) and the organic layer was washed with brine (20 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexane/Et_2O 40:1) to yield **46** (95 mg, 0.22 mmol, 83%) as a light red oil. $R_f = 0.6$ (hexane/Et_2O 40:1). IR (CH_2Cl_2, cast) 3096, 2955, 2934, 2911, 2874, 2210, 2160, 1457, 1413, 1378 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.40-4.60 (m, 2H), 4.05-4.40 (m, 7H), 1.01 (t, J = 7.8 Hz, 9H), 0.65 (q, J = 7.8 Hz, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 134.5, 107.7, 100.2, 99.5, 96.3, 79.9, 71.8, 70.2, 69.5, 63.7, 7.4, 4.2; EIMS *m/z* 442 (M^+, 100); HRMS calcd. for $C_{22}H_{24}Si^{35}Cl_2Fe$ (M^+) 442.0373, found 442.0371



3-Dichloromethylidene-1,6-triisopropylsilyl-penta-1,4-diyne (48)

To a stirred solution of the diethynyl ketone **47**[77] (1.00 g, 2.56 mmol) in CH_3CN (20 mL), was added sequentially PPh_3 (2.68 g, 10.2 mmol) and CCl_4 (708 mg, 5.12 mmol). The mixture was stirred at rt for 2 h then poured into H_2O (50 mL). The resulting solution was extracted with Et_2O (2 x 20 mL) and the organic layer washed with brine (20 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was purified by flash column chromatography (silica gel, hexanes) to yield **48** (971 mg, 2.13 mmol, 83%) as a light orange oil. $R_f = 0.7$ (hexanes). IR (neat)

2943, 2891, 2866, 2725, 2155, 1536, 1463, 1383, 1366 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.05-1.50 (m, 42H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$, APT) δ 136.5, 108.0, 100.35, 100.32, 18.6, 11.5; EIMS *m/z* 456 (M$^+$, 27), 413 ([M – *i*-Pr]$^+$, 100); HRMS calcd. for $C_{24}H_{42}Si_2{}^{35}Cl_2$ (M$^+$) 456.2202, found 456.2206. Anal. calcd. for $C_{24}H_{42}Si_2Cl_2$: C; 63.16, H; 9.21. Found: C; 63.04, H; 9.41.

Attempted Rearrangement of Dichloride 48

Dichloride **48** (100 mg, 0.22 mmol) was dissolved in hexanes (5 mL) and cooled to –78 °C. To this was added *n*-BuLi (0.10 mL, 0.24 mmol), the mixture stirred at –78 °C for 30 min, then warmed to rt. The mixture was poured into H_2O (10 mL), the organic layer washed with brine (10 mL), dried (Na_2SO_4), filtered, and evaporated. Starting material was recovered (98 mg, 0.21 mmol, 98%) and no product formation was evident.

Other attempted conditions: *n*-BuLi in Et_2O or THF, at –78 °C or rt, effected mixtures of protonated starting material, and starting material. *n*-BuLi in toluene or benzene, at –78 °C or rt, effected mixtures of rearranged product, butylated product, and starting material. *t*-BuLi in toluene, at –78 °C, effected mixtures of starting material and rearranged product. Inverse addition of dichloride **48** to a solution of excess *n*-BuLi effected starting material decomposition.

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VI APPENDIX

1 Crystal Structure Data for Vinyl Acetate 14

Analysis performed by Meitian Wang. For details of the X-ray structure see Dr. Robert McDonald, X-ray crystallography laboratory, University of Alberta.

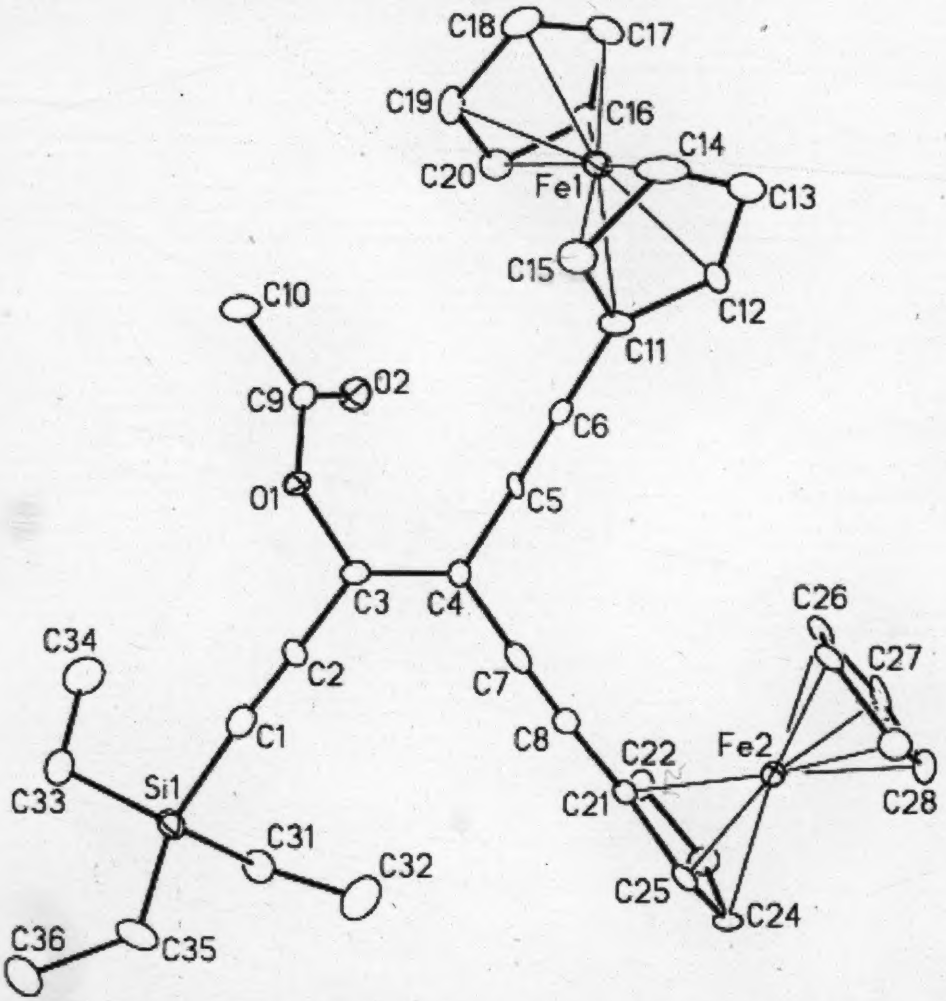

C18
C17
C19
C16
C14
C20
Fe1
C13
C15
C10
C12
C11
C9
O2
C6
O1
C5
C3
C4
C26
C34
C2
C7
C27
C1
C8
C22
Fe2
C33
Si1
C21
C28
C31
C32
C25
C24
C36
C35

Figure 8. Perspective view of one of the two crystallographically-independent molecules of Vinyl Acetate **14** $(Et_3SiC{\equiv}C)(AcO)C{=}C(C{\equiv}CC_5H_4FeCp)_2$ (molecule A) showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are not shown.

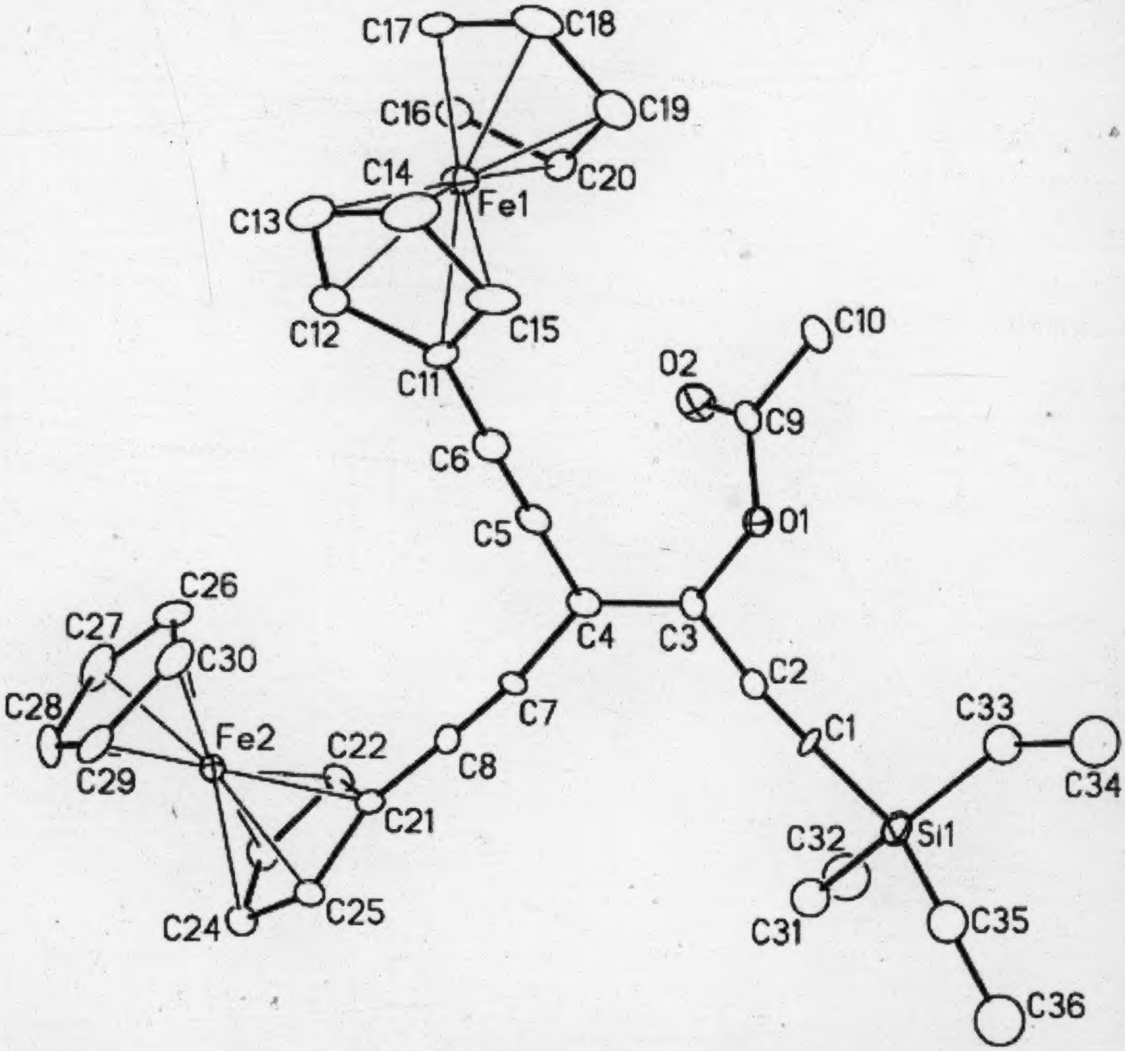

C17
C18
C16
C19
C14
C20
Fe1
C13
C12
C15
C10
C11
O2
C9
C6
O1
C5
C26
C27
C30
C4
C3
C2
C28
C7
C33
Fe2
C22
C1
C29
C8
C34
C21
C32
Si1
C24
C25
C31
C35
C36

Figure 9. Perspective view of the second crystallographically-independent molecule of Vinyl Acetate **14** $(Et_3SiC{\equiv}C)(AcO)C{=}C(C{\equiv}CC_5H_4FeCp)_2$ (molecule B).

Table A1. Crystallographic Experimental Details

A. Crystal Data	
formula	$C_{36}H_{36}Fe_2O_2Si$
formula weight	640.44
crystal dimensions (mm)	0.29 × 0.13 × 0.04
crystal system	orthorhombic
space group	$P2_12_12_1$ (No. 19)
unit cell parameters[a]	
a (Å)	12.7691 (6)
b (Å)	11.8154 (5)
c (Å)	41.2882 (18)
V (Å^3)	6229.2 (5)
Z 8	
_calcd (g cm^{-3})	1.366
μ (mm^{-1})	1.001
B. Data Collection and Refinement Conditions	
diffractometer	Bruker PLATFORM/SMART 1000 CCD[b]
radiation (λ [Å]) (0.71073)	graphite-monochromated Mo K_
temperature (°C)	–80
scan type	ω scans (0.2°) (30 s exposures)
data collection 2θ limit (deg)	52.78
total data collected	26535 ($-15 \le h \le 15$, $-11 \le k \le 14$, $-31 \le l \le 51$)
independent reflections	12604
number of observed reflections (*NO*)	7062 [$F_o^2 \ge 2\sigma(F_o^2)$]
structure solution method	direct methods (*SHELXS–86*[c])
refinement method (*SHELXL–93*[d])	full-matrix least-squares on F^2
absorption correction method	*SADABS*
range of transmission factors	0.9611–0.7601
data/restraints/parameters	12604 [$F_o^2 \ge -3\sigma(F_o^2)$] / 18[e] / 727
extinction coefficient (*x*)[f]	0.00043(10)
Flack absolute structure parameter[g]	0.27(3)
goodness-of-fit (*S*)[h]	0.998 [$F_o^2 \ge -3\sigma(F_o^2)$]
final *R* indices[i]	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0707
wR_2 [$F_o^2 \ge -3\sigma(F_o^2)$]	0.1686
largest difference peak and hole	1.166 and –0.474 e Å^{-3}

[a] Obtained from least-squares refinement of 6049 centered reflections.

Table A1. Crystallographic Experimental Details (continued)

[b] Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c] Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467–473.

[d] Sheldrick, G. M. *SHELXL-93*. Program for crystal structure determination. University of Göttingen, Germany, 1993. Refinement on F_o^2 for all reflections (all of these having $F_o^2 \geq -3\sigma(F_o^2)$). Weighted *R*-factors wR_2 and all goodnesses of fit *S* are based on F_o^2; conventional *R*-factors R_1 are based on F_o, with F_o set to zero for negative F_o^2. The observed criterion of $F_o^2 > 2\sigma(F_o^2)$ is used only for calculating R_1, and is not relevant to the choice of reflections for refinement. *R*-factors based on F_o^2 are statistically about twice as large as those based on F_o, and *R*-factors based on ALL data will be even larger.

[e] An idealized geometry was imposed upon the disordered triethylsilyl group of molecule B by setting d(Si–C) = 1.85 Å, d(C–C) = 1.54 Å, and d(Si···C[methyl]) = 2.77 Å.

[f] $F_c^* = kF_c[1 + x\{0.001F_c^2\_^3/\sin(2\theta)\}]^{-1/4}$ where *k* is the overall scale factor.

[g] Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876–881. The Flack parameter will refine to a value near zero if the structure is in the correct configuration and will refine to a value near one for the inverted configuration. In this case the value of the Flack parameter is indicative of a moderate degree of racemic twinning, which has been handled through use of the *SHELXL-93* TWIN instruction.

[h] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0689P)^2]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[i] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table A4. Selected Interatomic Angles (continued)

(a) Molecule A(b) Molecule B

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C16	Fe1	C19	68.8(4)	C25	Fe2	C26	149.1(5)
C16	Fe1	C20	41.2(3)	C25	Fe2	C27	167.7(4)
C17	Fe1	C18	40.1(4)	C25	Fe2	C28	128.8(4)
C17	Fe1	C19	67.6(4)	C17	Fe1	C18	40.5(4)
C17	Fe1	C20	67.6(4)	C17	Fe1	C19	68.8(4)
C18	Fe1	C19	39.8(4)	C17	Fe1	C20	69.6(3)
C18	Fe1	C20	67.3(4)	C18	Fe1	C19	40.4(4)
C19	Fe1	C20	40.5(3)	C18	Fe1	C20	68.6(4)
C21	Fe2	C22	40.9(3)	C19	Fe1	C20	40.9(3)
C21	Fe2	C23	68.8(3)	C21	Fe2	C22	40.6(3)
C21	Fe2	C24	67.7(4)	C21	Fe2	C23	68.2(3)
C21	Fe2	C25	41.3(3)	C21	Fe2	C24	68.6(4)
C21	Fe2	C26	115.9(4)	C21	Fe2	C25	41.1(3)
C21	Fe2	C27	150.6(4)	C21	Fe2	C26	115.8(4)
C21	Fe2	C28	166.7(4)	C21	Fe2	C27	148.5(4)
C21	Fe2	C29	128.1(4)	C21	Fe2	C28	169.8(4)
C21	Fe2	C30	107.1(4)	C21	Fe2	C29	130.8(4)
C22	Fe2	C23	40.6(3)	C21	Fe2	C30	108.2(4)
C22	Fe2	C24	67.5(4)	C22	Fe2	C23	41.0(3)
C22	Fe2	C25	68.9(4)	C22	Fe2	C24	68.4(3)
C22	Fe2	C26	108.1(4)	C22	Fe2	C25	68.9(3)
C22	Fe2	C27	118.5(4)	C22	Fe2	C26	109.0(4)
C22	Fe2	C28	151.8(4)	C22	Fe2	C27	116.7(4)
C22	Fe2	C29	166.9(4)	C22	Fe2	C28	149.2(4)
C22	Fe2	C30	128.8(4)	C22	Fe2	C29	169.3(4)
C23	Fe2	C24	40.5(3)	C22	Fe2	C30	130.7(4)
C23	Fe2	C25	68.8(4)	C23	Fe2	C24	39.7(4)
C23	Fe2	C26	130.1(4)	C23	Fe2	C25	68.2(4)
C23	Fe2	C27	109.7(4)	C23	Fe2	C26	132.5(4)
C23	Fe2	C28	118.9(4)	C23	Fe2	C27	109.9(5)
C23	Fe2	C29	151.0(4)	C23	Fe2	C28	117.6(4)
C23	Fe2	C30	167.4(4)	C23	Fe2	C29	148.7(4)
C24	Fe2	C25	39.8(4)	C23	Fe2	C30	170.6(4)
C24	Fe2	C26	169.5(5)	C24	Fe2	C25	41.1(4)
C24	Fe2	C27	131.4(5)	C24	Fe2	C26	170.5(5)
C24	Fe2	C28	110.4(4)	C24	Fe2	C27	131.2(5)
C24	Fe2	C29	118.1(4)	C24	Fe2	C28	109.9(4)
C24	Fe2	C30	150.2(4)	C24	Fe2	C29	116.9(4)

Table A2. Atomic Coordinates and Displacement Parameters (continued)

Atom	x	y	z	U_{eq}, Å^2
C33	-0.2976(6)	0.1890(8)	-0.2844(2)	0.051(2)*
C34	-0.2006(8)	0.1733(10)	-0.2628(3)	0.079(3)*
C35	-0.5386(8)	0.2195(8)	-0.2881(2)	0.056(3)*
C36	-0.5166(8)	0.2283(10)	-0.3249(2)	0.071(3)*

(b) Molecule B

Atom	x	y	z	U_{eq}, Å^2
Fe1	-0.17549(9)	0.17995(11)	-0.05358(3)	0.0331(3)*
Fe2	0.18402(8)	-0.42907(9)	-0.08503(3)	0.0263(3)*
Si1	-0.1164(2)	-0.2825(2)	-0.27070(6)	0.0512(7)*
O1	-0.1586(4)	-0.0001(5)	-0.17806(13)	0.0329(15)*
O2	-0.2806(5)	-0.0771(6)	-0.14541(18)	0.0497(19)*
C1	-0.1043(6)	-0.2102(7)	-0.23109(18)	0.0283(19)*
C2	-0.0984(6)	-0.1646(7)	-0.2061(2)	0.0280(19)*
C3	-0.0970(6)	-0.0956(7)	-0.1765(2)	0.0260(19)*
C4	-0.0419(6)	-0.1167(7)	-0.1495(2)	0.027(2)*
C5	-0.0435(6)	-0.0369(8)	-0.1235(2)	0.028(2)*
C6	-0.0459(6)	0.0299(8)	-0.1017(2)	0.033(2)*
C7	0.0234(6)	-0.2156(7)	-0.14594(19)	0.0232(19)*
C8	0.0747(6)	-0.2973(7)	-0.13915(18)	0.0256(19)*
C9	-0.2478(6)	0.0047(8)	-0.1595(2)	0.030(2)*
C10	-0.2964(8)	0.1194(8)	-0.1618(2)	0.051(3)*
C11	-0.0470(6)	0.1143(8)	-0.0766(2)	0.032(2)*
C12	-0.0414(7)	0.0935(10)	-0.0424(3)	0.044(3)*
C13	-0.0425(7)	0.2005(12)	-0.0269(3)	0.062(4)*
C14	-0.0503(7)	0.2845(11)	-0.0504(3)	0.062(3)*
C15	-0.0539(7)	0.2339(8)	-0.0811(3)	0.046(3)*
C16	-0.2990(6)	0.0846(8)	-0.0385(2)	0.036(2)*
C17	-0.2994(7)	0.1932(9)	-0.0227(2)	0.044(3)*
C18	-0.3072(7)	0.2762(9)	-0.0472(3)	0.051(3)*
C19	-0.3101(7)	0.2229(9)	-0.0780(3)	0.049(3)*
C20	-0.3048(6)	0.1029(8)	-0.0729(2)	0.032(2)*
C21	0.1330(6)	-0.3969(7)	-0.1306(2)	0.025(2)*
C22	0.0865(6)	-0.4967(8)	-0.1188(2)	0.033(2)*
C23	0.1690(8)	-0.5763(7)	-0.1120(2)	0.039(2)*
C24	0.2644(7)	-0.5223(8)	-0.1184(3)	0.042(3)*
C25	0.2443(6)	-0.4106(8)	-0.1307(2)	0.031(2)*
C26	0.0980(7)	-0.3624(11)	-0.0492(3)	0.061(4)*
C27	0.1488(9)	-0.4606(12)	-0.0380(2)	0.063(4)*
C28	0.2557(7)	-0.4409(9)	-0.0409(3)	0.047(3)*

Table A2. Atomic Coordinates and Displacement Parameters (continued)

Atom	x	y	z	U_{eq}, Å^2
C29	0.2716(7)	-0.3320(9)	-0.0536(2)	0.043(3)*
C30	0.1725(9)	-0.2838(9)	-0.0588(2)	0.052(3)*
C31[a,b]	-0.0700(11)	-0.4294(5)	-0.2648(5)	0.058(2)
C32[a,c]	-0.1561(16)	-0.5123(4)	-0.2757(6)	0.093(3)
C33[a,b]	-0.2487(9)	-0.2461(17)	-0.2858(7)	0.058(2)
C34[a,c]	-0.244(2)	-0.130(3)	-0.3040(18)	0.093(3)
C35[a,b]	-0.0176(11)	-0.2005(12)	-0.2936(4)	0.058(2)
C36[a,c]	0.0078(16)	-0.263(2)	-0.3254(3)	0.093(3)
C31'[a,b]	-0.1359(15)	-0.4336(4)	-0.2606(3)	0.058(2)
C32'[a,c]	-0.150(2)	-0.5017(7)	-0.2921(4)	0.093(3)
C33'[a,b]	-0.2449(11)	-0.2521(18)	-0.2896(7)	0.058(2)
C34'[a,c]	-0.265(3)	-0.121(2)	-0.2887(18)	0.093(3)
C35'[a,b]	0.0034(7)	-0.2462(18)	-0.2937(3)	0.058(2)
C36'[a,c]	-0.0229(15)	-0.240(2)	-0.3300(3)	0.093(3)

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$. [a] Refined with an occupancy factor of 0.5. [b] The methylene carbons of this disordered $SiEt_3$ group were refined with a common isotropic displacement parameter. [c] The methyl carbons of this disordered $SiEt_3$ group were refined with a common isotropic displacement parameter.

Table A3. Selected Interatomic Distances (Å)

(a) Molecule A			*(b) Molecule B*		
Atom1	Atom2	Distance	Atom1	Atom2	Distance
Fe1	C11	2.040(8)	C8	C21	1.437(11)
Fe1	C12	2.032(9)	Fe1	C11	2.048(8)
Fe1	C13	2.046(9)	Fe1	C12	2.047(10)
Fe1	C14	2.047(9)	Fe1	C13	2.038(10)
Fe1	C15	2.040(9)	Fe1	C14	2.025(10)
Fe1	C16	2.031(9)	Fe1	C15	2.027(9)
Fe1	C17	2.041(8)	Fe1	C16	2.035(9)
Fe1	C18	2.015(9)	Fe1	C17	2.038(9)
Fe1	C19	2.036(8)	Fe1	C18	2.047(10)
Fe1	C20	2.030(9)	Fe1	C19	2.056(10)
Fe2	C21	2.048(8)	Fe1	C20	2.047(8)
Fe2	C22	2.029(9)	Fe2	C21	2.028(9)
Fe2	C23	2.031(9)	Fe2	C22	2.032(9)
Fe2	C24	2.062(9)	Fe2	C23	2.075(8)
Fe2	C25	2.014(9)	Fe2	C24	2.042(10)
Fe2	C26	2.046(9)	Fe2	C25	2.049(10)
Fe2	C27	2.043(9)	Fe2	C26	2.003(10)
Fe2	C28	2.030(10)	Fe2	C27	2.027(10)
Fe2	C29	2.033(10)	Fe2	C28	2.046(10)
Fe2	C30	2.035(9)	Fe2	C29	2.060(9)
Si1	C1	1.859(9)	Fe2	C30	2.034(9)
Si1	C31	1.875(8)	Si1	C1	1.851(8)
Si1	C33	1.859(8)	Si1	C31	1.85†
Si1	C35	1.877(9)	Si1	C33	1.85†
			Si1	C35	1.85†
			Si1	C31'	1.85†
			Si1	C33'	1.85†
O1	C3	1.420(9)	Si1	C35'	1.85†
O1	C9	1.397(10)	O1	C3	1.377(9)
O2	C9	1.190(12)	O1	C9	1.374(10)
C1	C2	1.221(11)	O2	C9	1.204(11)
C2	C3	1.381(10)	C1	C2	1.167(11)
C3	C4	1.352(11)	C2	C3	1.468(11)
C4	C5	1.429(11)	C3	C4	1.341(11)
C4	C7	1.432(11)	C4	C5	1.430(12)
C5	C6	1.195(10)	C4	C7	1.443(10)
C6	C11	1.423(12)	C5	C6	1.198(11)
C7	C8	1.170(11)	C6	C11	1.439(13)

Table A3. Selected Interatomic Distances (continued)

(a) Molecule A

Atom1	Atom2	Distance
C7	C8	1.200(10)
C8	C21	1.436(11)
C9	C10	1.475(13)
C11	C12	1.436(13)
C11	C15	1.450(12)
C12	C13	1.394(14)
C13	C14	1.431(15)
C14	C15	1.449(14)
C16	C17	1.410(13)
C16	C20	1.404(11)
C17	C18	1.389(12)
C18	C19	1.380(12)
C19	C20	1.406(12)
C21	C22	1.425(12)
C21	C25	1.432(11)
C22	C23	1.408(11)
C23	C24	1.418(12)
C24	C25	1.388(13)
C26	C27	1.437(15)
C26	C30	1.393(14)
C27	C28	1.405(13)
C28	C29	1.391(14)
C29	C30	1.413(12)
C31	C32	1.550(12)
C33	C34	1.537(12)
C35	C36	1.545(12)

(b) Molecule B

Atom1	Atom2	Distance
C9	C10	1.493(12)
C11	C12	1.437(14)
C11	C15	1.428(12)
C12	C13	1.416(15)
C13	C14	1.389(16)
C14	C15	1.403(14)
C16	C17	1.440(13)
C16	C20	1.437(12)
C17	C18	1.414(13)
C18	C19	1.418(13)
C19	C20	1.435(12)
C21	C22	1.408(12)
C21	C25	1.430(10)
C22	C23	1.440(11)
C23	C24	1.400(13)
C24	C25	1.437(14)
C26	C27	1.407(15)
C26	C30	1.387(14)
C27	C28	1.390(12)
C28	C29	1.406(14)
C29	C30	1.403(14)
C31	C32	1.54†
C33	C34	1.54†
C35	C36	1.54†
C31'	C32'	1.54†
C33'	C34'	1.54†
C35'	C36'	1.54†

†Distance fixed during refinement.

Table A4. Selected Interatomic Angles (deg)

(a) Molecule A				*(b) Molecule B*			
Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C11	Fe1	C12	41.3(4)	C16	Fe1	C20	40.5(3)
C11	Fe1	C13	68.3(4)	C11	Fe1	C12	41.1(4)
C11	Fe1	C14	69.2(4)	C11	Fe1	C13	68.2(4)
C11	Fe1	C15	41.6(3)	C11	Fe1	C14	68.2(4)
C11	Fe1	C16	124.6(4)	C11	Fe1	C15	41.0(3)
C11	Fe1	C17	161.9(4)	C11	Fe1	C16	123.6(4)
C11	Fe1	C18	156.1(4)	C11	Fe1	C17	160.2(4)
C11	Fe1	C19	121.0(4)	C11	Fe1	C18	158.1(4)
C11	Fe1	C20	107.6(3)	C11	Fe1	C19	122.4(4)
C12	Fe1	C13	40.0(4)	C11	Fe1	C20	107.3(3)
C12	Fe1	C14	68.9(4)	C12	Fe1	C13	40.6(4)
C12	Fe1	C15	70.1(4)	C12	Fe1	C14	68.2(5)
C12	Fe1	C16	107.7(4)	C12	Fe1	C15	69.1(4)
C12	Fe1	C17	125.0(4)	C12	Fe1	C16	107.6(4)
C12	Fe1	C18	161.6(4)	C12	Fe1	C17	123.1(4)
C12	Fe1	C19	156.9(4)	C12	Fe1	C18	159.3(5)
C12	Fe1	C20	121.7(4)	C12	Fe1	C19	159.0(4)
C13	Fe1	C14	40.9(4)	C12	Fe1	C20	122.7(4)
C13	Fe1	C15	69.4(4)	C13	Fe1	C14	40.0(5)
C13	Fe1	C16	121.5(4)	C13	Fe1	C15	68.1(5)
C13	Fe1	C17	108.7(3)	C13	Fe1	C16	123.1(5)
C13	Fe1	C18	125.9(4)	C13	Fe1	C17	107.4(4)
C13	Fe1	C19	161.6(4)	C13	Fe1	C18	123.3(4)
C13	Fe1	C20	156.6(4)	C13	Fe1	C19	158.7(5)
C14	Fe1	C15	41.6(4)	C13	Fe1	C20	159.3(5)
C14	Fe1	C16	156.4(4)	C14	Fe1	C15	40.5(4)
C14	Fe1	C17	121.1(4)	C14	Fe1	C16	158.3(4)
C14	Fe1	C18	107.7(4)	C14	Fe1	C17	121.6(4)
C14	Fe1	C19	124.2(5)	C14	Fe1	C18	107.5(4)
C14	Fe1	C20	161.2(5)	C14	Fe1	C19	122.8(5)
C15	Fe1	C16	161.2(4)	C14	Fe1	C20	159.1(4)
C15	Fe1	C17	155.7(4)	C15	Fe1	C16	159.9(4)
C15	Fe1	C18	120.2(4)	C15	Fe1	C17	157.1(4)
C15	Fe1	C19	106.1(4)	C15	Fe1	C18	121.8(4)
C15	Fe1	C20	123.8(4)	C15	Fe1	C19	106.8(4)
C16	Fe1	C17	40.5(3)	C15	Fe1	C20	122.7(4)
C16	Fe1	C18	67.8(4)	C16	Fe1	C17	41.4(4)
C16	Fe1	C19	68.2(4)	C16	Fe1	C18	68.4(4)

Table A4. Selected Interatomic Angles (continued)

(a) Molecule A(b) Molecule B

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C16	Fe1	C19	68.8(4)	C25	Fe2	C26	149.1(5)
C16	Fe1	C20	41.2(3)	C25	Fe2	C27	167.7(4)
C17	Fe1	C18	40.1(4)	C25	Fe2	C28	128.8(4)
C17	Fe1	C19	67.6(4)	C17	Fe1	C18	40.5(4)
C17	Fe1	C20	67.6(4)	C17	Fe1	C19	68.8(4)
C18	Fe1	C19	39.8(4)	C17	Fe1	C20	69.6(3)
C18	Fe1	C20	67.3(4)	C18	Fe1	C19	40.4(4)
C19	Fe1	C20	40.5(3)	C18	Fe1	C20	68.6(4)
C21	Fe2	C22	40.9(3)	C19	Fe1	C20	40.9(3)
C21	Fe2	C23	68.8(3)	C21	Fe2	C22	40.6(3)
C21	Fe2	C24	67.7(4)	C21	Fe2	C23	68.2(3)
C21	Fe2	C25	41.3(3)	C21	Fe2	C24	68.6(4)
C21	Fe2	C26	115.9(4)	C21	Fe2	C25	41.1(3)
C21	Fe2	C27	150.6(4)	C21	Fe2	C26	115.8(4)
C21	Fe2	C28	166.7(4)	C21	Fe2	C27	148.5(4)
C21	Fe2	C29	128.1(4)	C21	Fe2	C28	169.8(4)
C21	Fe2	C30	107.1(4)	C21	Fe2	C29	130.8(4)
C22	Fe2	C23	40.6(3)	C21	Fe2	C30	108.2(4)
C22	Fe2	C24	67.5(4)	C22	Fe2	C23	41.0(3)
C22	Fe2	C25	68.9(4)	C22	Fe2	C24	68.4(3)
C22	Fe2	C26	108.1(4)	C22	Fe2	C25	68.9(3)
C22	Fe2	C27	118.5(4)	C22	Fe2	C26	109.0(4)
C22	Fe2	C28	151.8(4)	C22	Fe2	C27	116.7(4)
C22	Fe2	C29	166.9(4)	C22	Fe2	C28	149.2(4)
C22	Fe2	C30	128.8(4)	C22	Fe2	C29	169.3(4)
C23	Fe2	C24	40.5(3)	C22	Fe2	C30	130.7(4)
C23	Fe2	C25	68.8(4)	C23	Fe2	C24	39.7(4)
C23	Fe2	C26	130.1(4)	C23	Fe2	C25	68.2(4)
C23	Fe2	C27	109.7(4)	C23	Fe2	C26	132.5(4)
C23	Fe2	C28	118.9(4)	C23	Fe2	C27	109.9(5)
C23	Fe2	C29	151.0(4)	C23	Fe2	C28	117.6(4)
C23	Fe2	C30	167.4(4)	C23	Fe2	C29	148.7(4)
C24	Fe2	C25	39.8(4)	C23	Fe2	C30	170.6(4)
C24	Fe2	C26	169.5(5)	C24	Fe2	C25	41.1(4)
C24	Fe2	C27	131.4(5)	C24	Fe2	C26	170.5(5)
C24	Fe2	C28	110.4(4)	C24	Fe2	C27	131.2(5)
C24	Fe2	C29	118.1(4)	C24	Fe2	C28	109.9(4)
C24	Fe2	C30	150.2(4)	C24	Fe2	C29	116.9(4)

Table A4. Selected Interatomic Angles (continued)

(a) Molecule A				*(b) Molecule B*			
Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C25	Fe2	C29	107.3(4)	C26	Fe2	C28	67.3(4)
C25	Fe2	C30	116.6(4)	C26	Fe2	C29	67.3(4)
C26	Fe2	C27	41.1(4)	C26	Fe2	C30	40.2(4)
C26	Fe2	C28	68.5(4)	C27	Fe2	C28	39.9(4)
C26	Fe2	C29	68.3(4)	C27	Fe2	C29	67.7(4)
C26	Fe2	C30	39.9(4)	C27	Fe2	C30	68.2(5)
C27	Fe2	C28	40.4(4)	C28	Fe2	C29	40.0(4)
C27	Fe2	C29	67.8(4)	C28	Fe2	C30	67.4(4)
C27	Fe2	C30	67.6(5)	C29	Fe2	C30	40.1(4)
C28	Fe2	C29	40.1(4)	C1	Si1	C31	106.8(6)
C28	Fe2	C30	67.6(4)	C1	Si1	C33	105.4(9)
C29	Fe2	C30	40.6(4)	C1	Si1	C35	98.8(6)
C1	Si1	C31	105.0(4)	C1	Si1	C31'	104.9(5)
C1	Si1	C33	107.4(4)	C1	Si1	C33'	110.9(9)
C1	Si1	C35	109.2(4)	C1	Si1	C35'	106.1(6)
				C31	Si1	C33	123.7(8)
				C31	Si1	C35	109.9(8)
C31	Si1	C33	111.6(4)	C33	Si1	C35	109.2(10)
C31	Si1	C35	111.0(4)	C31'	Si1	C33'	99.4(9)
C33	Si1	C35	112.3(4)	C31'	Si1	C35'	116.8(9)
C3	O1	C9	116.3(7)	C33'	Si1	C35'	118.1(10)
Si1	C1	C2	174.6(8)	C3	O1	C9	118.8(7)
C1	C2	C3	179.2(9)	Si1	C1	C2	179.0(7)
O1	C3	C2	114.1(7)	C1	C2	C3	173.1(9)
O1	C3	C4	118.9(7)	O1	C3	C2	114.2(7)
C2	C3	C4	126.7(8)	O1	C3	C4	119.4(7)
C3	C4	C5	121.5(8)	C2	C3	C4	126.4(8)
C3	C4	C7	120.0(8)	C3	C4	C5	119.6(8)
C5	C4	C7	118.4(7)	C3	C4	C7	122.7(8)
C4	C5	C6	176.7(9)	C5	C4	C7	117.7(8)
C5	C6	C11	177.5(9)	C4	C5	C6	179.3(9)
C4	C7	C8	176.9(9)	C5	C6	C11	177.2(10)
C7	C8	C21	175.9(9)	C4	C7	C8	172.3(9)
O1	C9	O2	123.3(9)	C7	C8	C21	178.1(9)
O1	C9	C10	108.8(9)	O1	C9	O2	121.7(8)
C25	Fe2	C29	108.4(4)	O1	C9	C10	110.3(8)
C25	Fe2	C30	115.3(4)				
C26	Fe2	C27	40.9(5)				

Table A4. Selected Interatomic Angles (continued)

(a) Molecule A				*(b) Molecule B*			
Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
O2	C9	C10	127.7(9)	C8	C21	C25	128.0(8)
Fe1	C11	C6	125.6(6)	O2	C9	C10	127.9(9)
Fe1	C11	C12	69.0(5)	Fe1	C11	C6	127.2(6)
Fe1	C11	C15	69.2(5)	Fe1	C11	C12	69.4(5)
C6	C11	C12	126.9(9)	Fe1	C11	C15	68.7(5)
C6	C11	C15	124.8(9)	C6	C11	C12	126.1(9)
C12	C11	C15	108.2(9)	C6	C11	C15	126.4(9)
Fe1	C12	C11	69.7(5)	C12	C11	C15	107.5(9)
Fe1	C12	C13	70.5(6)	Fe1	C12	C11	69.5(5)
C11	C12	C13	108.2(10)	Fe1	C12	C13	69.4(6)
Fe1	C13	C12	69.5(5)	C11	C12	C13	106.8(10)
Fe1	C13	C14	69.6(5)	Fe1	C13	C12	70.1(6)
C12	C13	C14	109.4(9)	Fe1	C13	C14	69.5(6)
Fe1	C14	C13	69.5(6)	C12	C13	C14	109.0(10)
Fe1	C14	C15	69.0(5)	Fe1	C14	C13	70.5(6)
C13	C14	C15	107.7(9)	Fe1	C14	C15	69.8(5)
Fe1	C15	C11	69.2(5)	C13	C14	C15	109.1(11)
Fe1	C15	C14	69.5(5)	Fe1	C15	C11	70.3(5)
C11	C15	C14	106.3(10)	Fe1	C15	C14	69.6(6)
Fe1	C16	C17	70.1(5)	C11	C15	C14	107.6(11)
Fe1	C16	C20	69.7(5)	Fe1	C16	C17	69.4(5)
C17	C16	C20	107.2(9)	Fe1	C16	C20	69.8(5)
Fe1	C17	C16	69.4(5)	C17	C16	C20	108.3(9)
Fe1	C17	C18	69.0(5)	Fe1	C17	C16	69.2(5)
C16	C17	C18	107.4(8)	Fe1	C17	C18	70.1(5)
Fe1	C18	C17	71.0(5)	C16	C17	C18	107.0(8)
Fe1	C18	C19	70.9(5)	Fe1	C18	C17	69.4(5)
C17	C18	C19	109.9(8)	Fe1	C18	C19	70.1(5)
Fe1	C19	C18	69.3(5)	C17	C18	C19	109.6(9)
Fe1	C19	C20	69.5(5)	Fe1	C19	C18	69.4(6)
C18	C19	C20	107.0(9)	Fe1	C19	C20	69.2(6)
Fe1	C20	C16	69.8(5)	C18	C19	C20	107.8(9)
Fe1	C20	C19	70.0(5)	Fe1	C20	C16	68.9(5)
C16	C20	C19	108.5(9)	Fe1	C20	C19	69.9(6)
Fe2	C21	C8	123.9(6)	C16	C20	C19	107.2(9)
Fe2	C21	C22	68.8(5)	Fe2	C21	C8	123.2(6)
Fe2	C21	C25	68.1(5)	Fe2	C21	C22	69.9(5)
C8	C21	C22	125.4(7)	Fe2	C21	C25	70.3(6)

Table A4. Slected Interatomic Angles (continued)

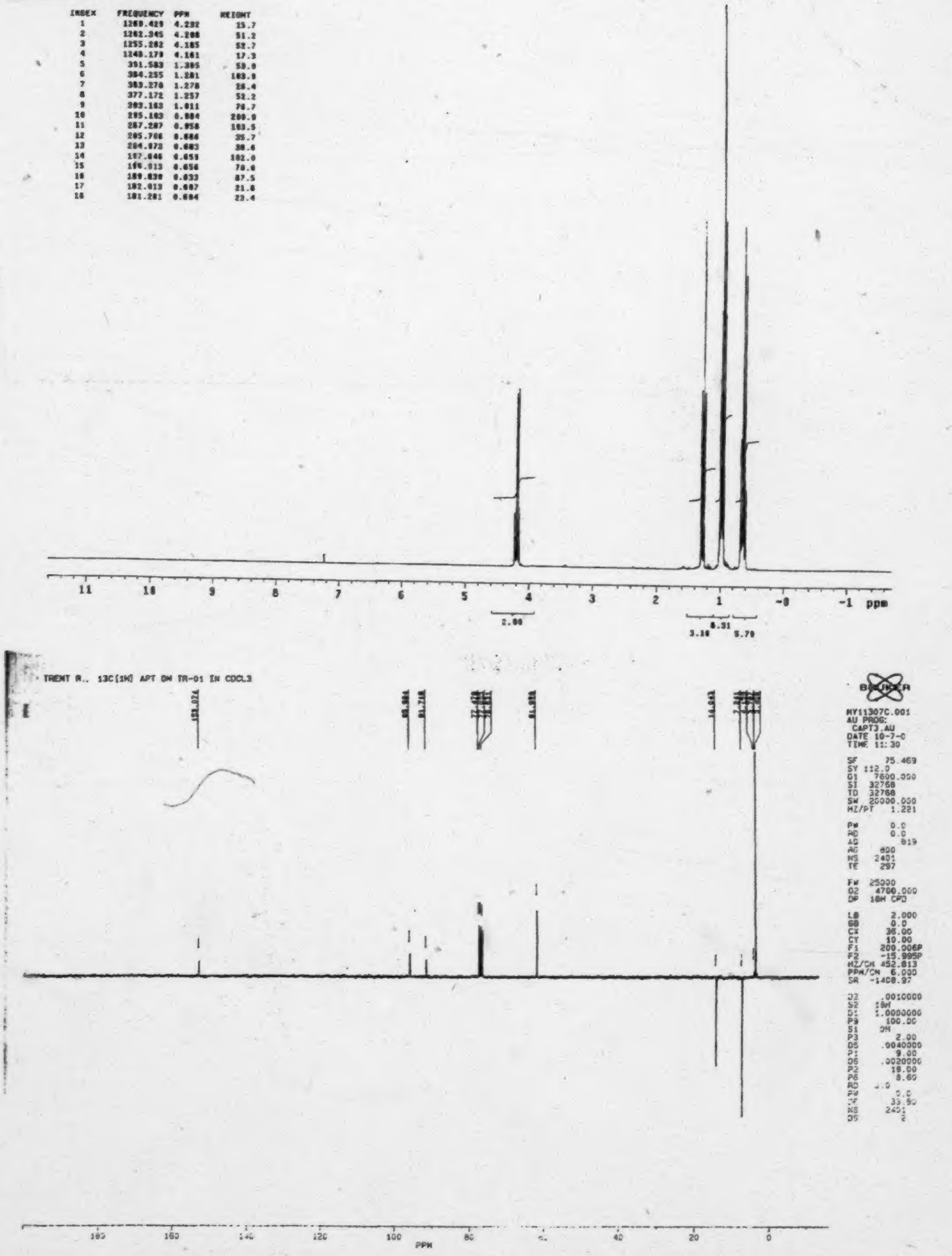
(a) Molecule A

Atom1	Atom2	Atom3	Angle
C22	C21	C25	106.3(8)
Fe2	C22	C21	70.3(5)
Fe2	C22	C23	69.8(5)
C21	C22	C23	108.9(8)
Fe2	C23	C22	69.6(5)
Fe2	C23	C24	70.9(5)
C22	C23	C24	107.2(8)
Fe2	C24	C23	68.6(5)
Fe2	C24	C25	68.2(5)
C23	C24	C25	109.0(8)
Fe2	C25	C21	70.7(5)
Fe2	C25	C24	72.0(6)
C21	C25	C24	108.4(8)
Fe2	C26	C27	69.3(6)
Fe2	C26	C30	69.6(5)
C27	C26	C30	106.6(8)
Fe2	C27	C26	69.6(5)
Fe2	C27	C28	69.3(6)
C26	C27	C28	107.7(11)
Fe2	C28	C27	70.3(6)
Fe2	C28	C29	70.1(6)
C27	C28	C29	108.7(10)
Fe2	C29	C28	69.9(6)
Fe2	C29	C30	69.8(5)
C28	C29	C30	107.5(9)
Fe2	C30	C26	70.5(6)
Fe2	C30	C29	69.6(5)
C26	C30	C29	109.4(9)
Si1	C31	C32	112.0(6)
Si1	C33	C34	113.9(6)
Si1	C35	C36	115.8(7)
C22	C21	C25	109.0(9)
Fe2	C22	C21	69.5(5)
Fe2	C22	C23	71.1(5)
C21	C22	C23	107.8(7)
Fe2	C23	C22	67.9(5)
Fe2	C23	C24	68.8(5)

(b) Molecule B

Angle	Atom1	Atom2	Atom3
C22	C23	C24	107.6(8)
Fe2	C24	C23	71.4(5)
Fe2	C24	C25	69.7(5)
C23	C24	C25	109.3(8)
Fe2	C25	C21	68.7(5)
Fe2	C25	C24	69.2(6)
C21	C25	C24	106.3(9)
Fe2	C26	C27	70.5(6)
Fe2	C26	C30	71.1(6)
C27	C26	C30	109.2(9)
Fe2	C27	C26	68.7(6)
Fe2	C27	C28	70.8(6)
C26	C27	C28	106.7(10)
Fe2	C28	C27	69.3(6)
Fe2	C28	C29	70.6(6)
C27	C28	C29	109.0(10)
Fe2	C29	C28	69.4(5)
Fe2	C29	C30	69.0(5)
C28	C29	C30	107.4(9)
Fe2	C30	C26	68.7(6)
Fe2	C30	C29	71.0(5)
C26	C30	C29	107.7(9)
Si1	C31	C32	109.26(9)
Si1	C33	C34	109.2(3)
Si1	C35	C36	109.23(9)
Si1	C31'	C32'	109.24(9)
Si1	C33'	C34'	109.1(3)
Si1	C35'	C36'	109.31(9)

2. NMR Spectra



INDEX	FREQUENCY	PPM	HEIGHT
1	1269.429	4.232	15.7
2	1262.345	4.208	51.2
3	1255.262	4.185	52.7
4	1248.179	4.161	17.3
5	391.583	1.305	53.0
6	384.255	1.281	103.9
7	383.278	1.278	26.4
8	377.172	1.257	52.2
9	303.163	1.011	76.7
10	295.103	0.984	200.0
11	287.287	0.958	103.5
12	205.766	0.686	35.7
13	204.873	0.683	38.6
14	197.646	0.659	102.0
15	196.813	0.656	70.6
16	189.830	0.633	87.5
17	182.013	0.607	21.8
18	181.201	0.604	23.4

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HZ/PT    1.221

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NS    2401
TE     297

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DP   16H CPD

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GB       0.0
CX      36.00
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F2     -15.995P
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PPM/CM  6.000
SR   -1408.97

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D6      .0020000
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NS      2401
DS         2
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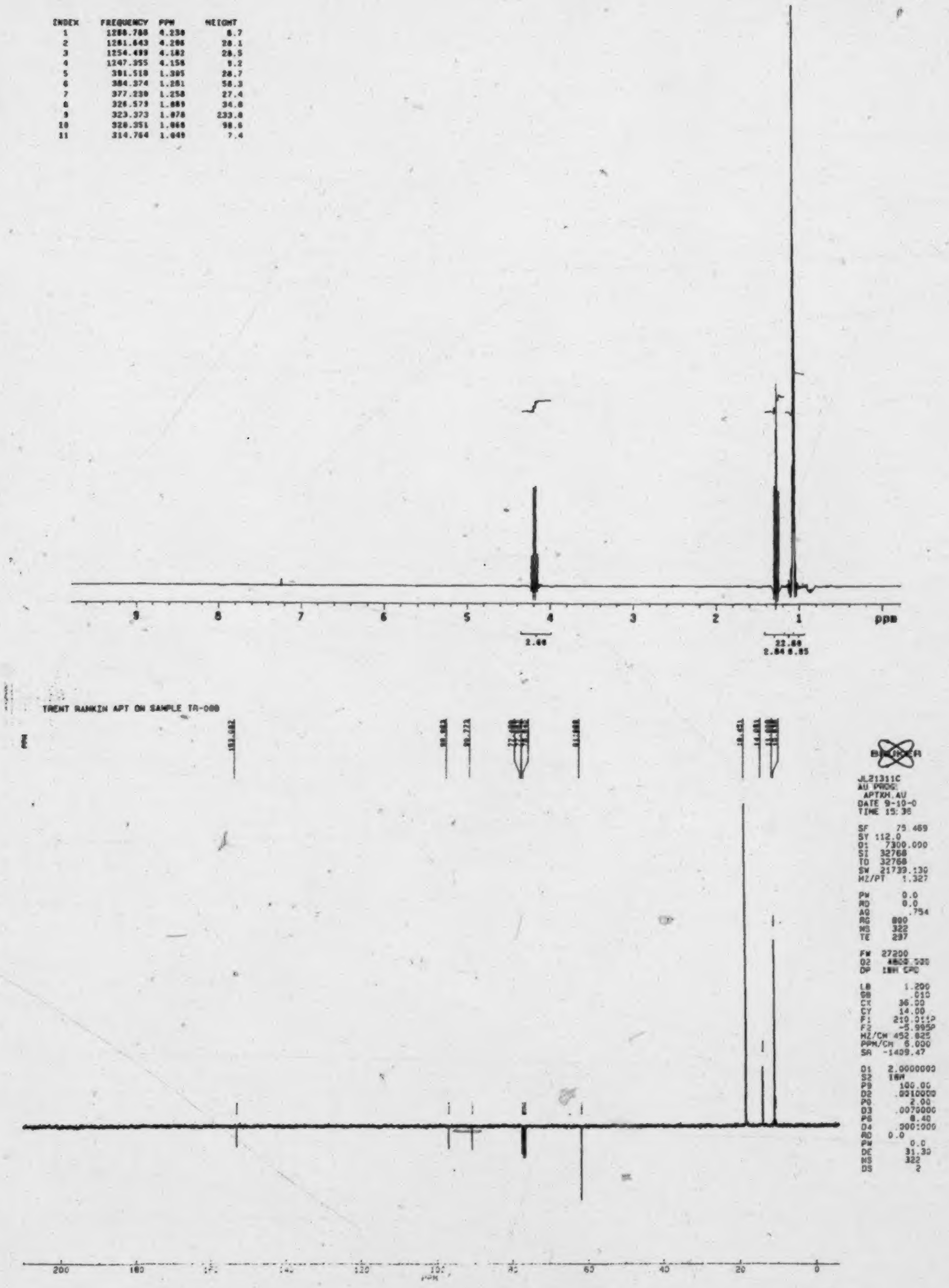
Figure 10. ^{1}H and ^{13}C NMR spectra of Compound 1



INDEX	FREQUENCY	PPM	HEIGHT
1	1268.788	4.230	8.7
2	1261.643	4.206	28.1
3	1254.499	4.182	28.5
4	1247.355	4.158	9.2
5	391.518	1.305	28.7
6	384.374	1.281	58.3
7	377.230	1.258	27.4
8	326.573	1.089	34.8
9	323.373	1.078	233.8
10	320.351	1.068	98.6
11	314.764	1.049	7.4

TRENT RANKIN APT ON SAMPLE TR-080

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AU PROG:
 APTXH.AU
DATE 9-10-0
TIME 15:36

SF      75.469
SY 112.0
O1    7300.000
SI   32768
TD   32768
SW   21739.130
HZ/PT    1.327

PW       0.0
RD       0.0
AQ        .754
RG     800
NS     322
TE     297

FW   27200
O2    4800.520
DP   18H CPD

LB       1.200
GB        .010
CX      36.00
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F2      -5.995P
HZ/CM 452.825
PPM/CM  6.000
SR   -1409.47

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P0        2.00
D3     .0070000
P6        8.40
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PW        0.0
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NS      322
DS        2
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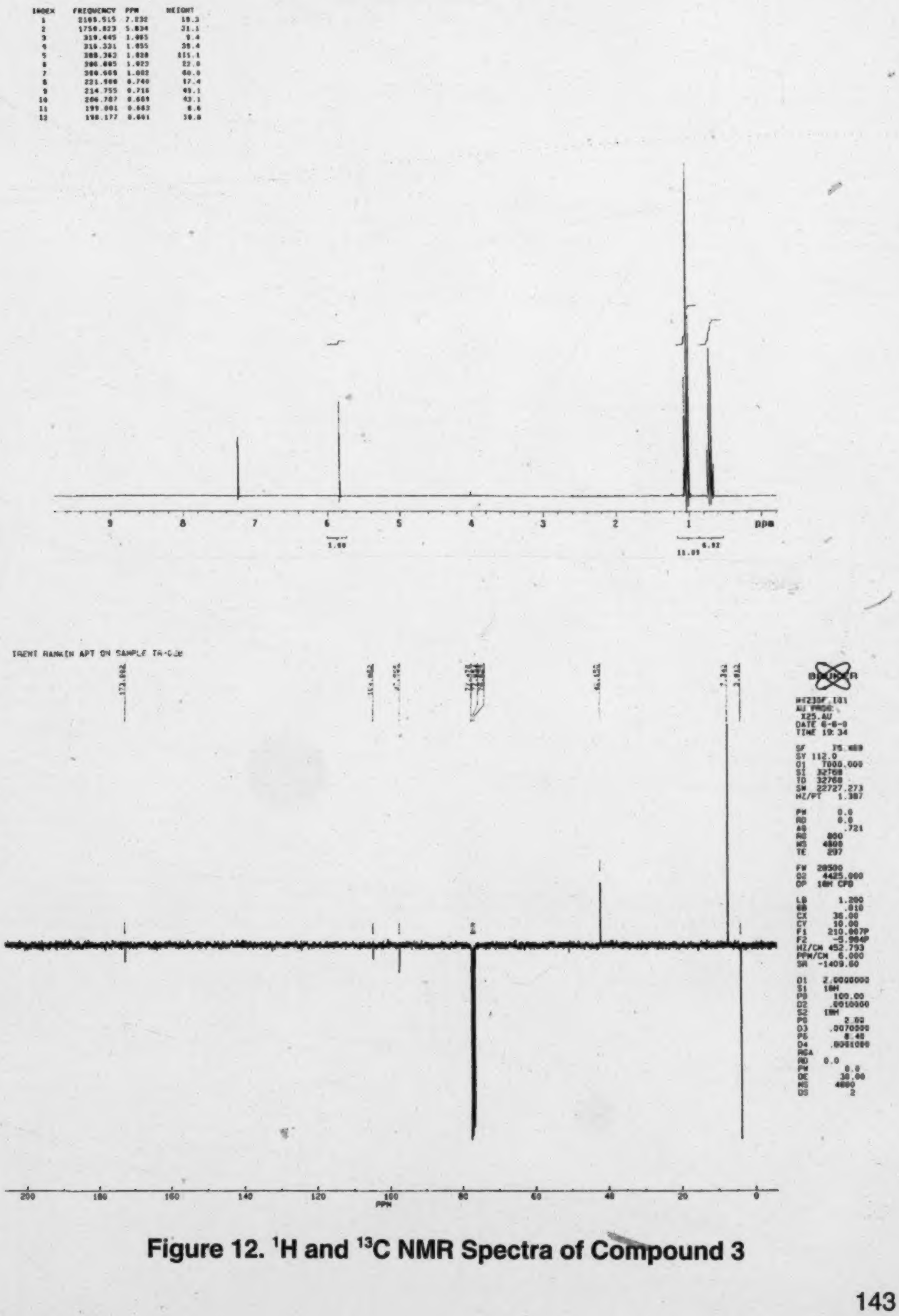
Figure 11. ^{1}H and ^{13}C NMR Spectra of Compound 2



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  1      2169.515  7.232      19.3
  2      1750.023  5.834      21.1
  3       319.445  1.065       9.4
  4       316.331  1.055      38.4
  5       308.363  1.028     111.1
  6       306.885  1.023      22.0
  7       300.669  1.002      60.0
  8       221.900  0.740      17.4
  9       214.755  0.716      49.1
 10       206.787  0.689      43.1
 11       199.001  0.663       8.6
 12       198.177  0.661      10.8
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TRENT RANKIN APT ON SAMPLE TR-03B

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O1    7000.000
SI   32768
TD   32768
SW   22727.273
HZ/PT    1.387

PW       0.0
RD       0.0
AQ        .721
RG     800
NS    4800
TE     297

FW   28500
O2    4425.000
DP   16H CPD

LB       1.200
GB        .010
CX      36.00
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F1     210.007P
F2      -5.984P
HZ/CM  452.793
PPM/CM   6.000
SR  -1409.60

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P9      100.00
D2     .0010000
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D3     .0070000
P6        8.40
D4     .0081000
RGA
RD   0.0
PW        0.0
DE       30.00
NS     4800
DS        2
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ppm
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7.361
3.012
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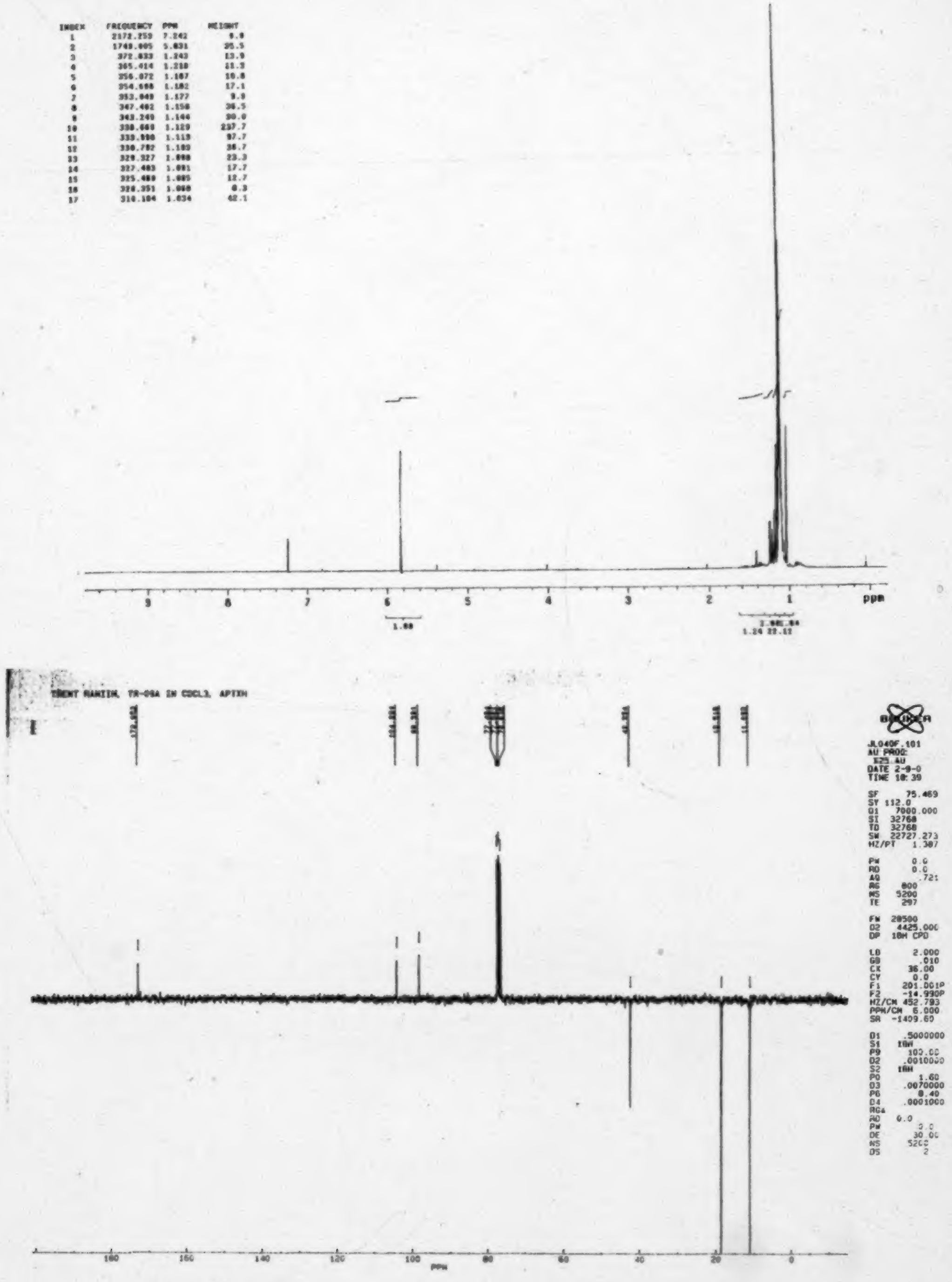
PPM

Figure 12. ^{1}H and ^{13}C NMR Spectra of Compound 3



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INDEX   FREQUENCY  PPM      HEIGHT
  1      2172.259  7.242      9.9
  2      1749.005  5.831     25.5
  3       372.833  1.243     13.9
  4       365.414  1.218     11.3
  5       356.072  1.187     10.8
  6       354.608  1.182     17.1
  7       353.049  1.177      9.9
  8       347.402  1.158     36.5
  9       343.249  1.144     30.0
 10       338.660  1.129    237.7
 11       333.990  1.113     97.7
 12       330.782  1.103     38.7
 13       329.327  1.098     23.3
 14       327.403  1.091     17.7
 15       325.480  1.085     12.7
 16       320.351  1.068      8.3
 17       310.104  1.034     42.1
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DATE 2-9-0
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SI   32768
TD   32768
SW   22727.273
HZ/PT    1.387

PW        0.0
RD        0.0
AQ         .721
RG      800
NS     5200
TE      297

FW   28500
O2    4425.000
DP   10H CPD

LB        2.000
GB         .010
CX       36.00
CY        0.0
F1      201.001P
F2      -14.990P
HZ/CM 452.793
PPM/CM   6.000
SR   -1409.60

D1       .5000000
S1     10H
P9      100.00
D2       .0010000
S2     10H
P0        1.60
D3       .0070000
P6        8.40
D4       .0001000
RGA
RD     0.0
PW        0.0
DE       30.00
NS     5200
DS        2
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Figure 13. ^{1}H and ^{13}C NMR Spectra of Compound 4

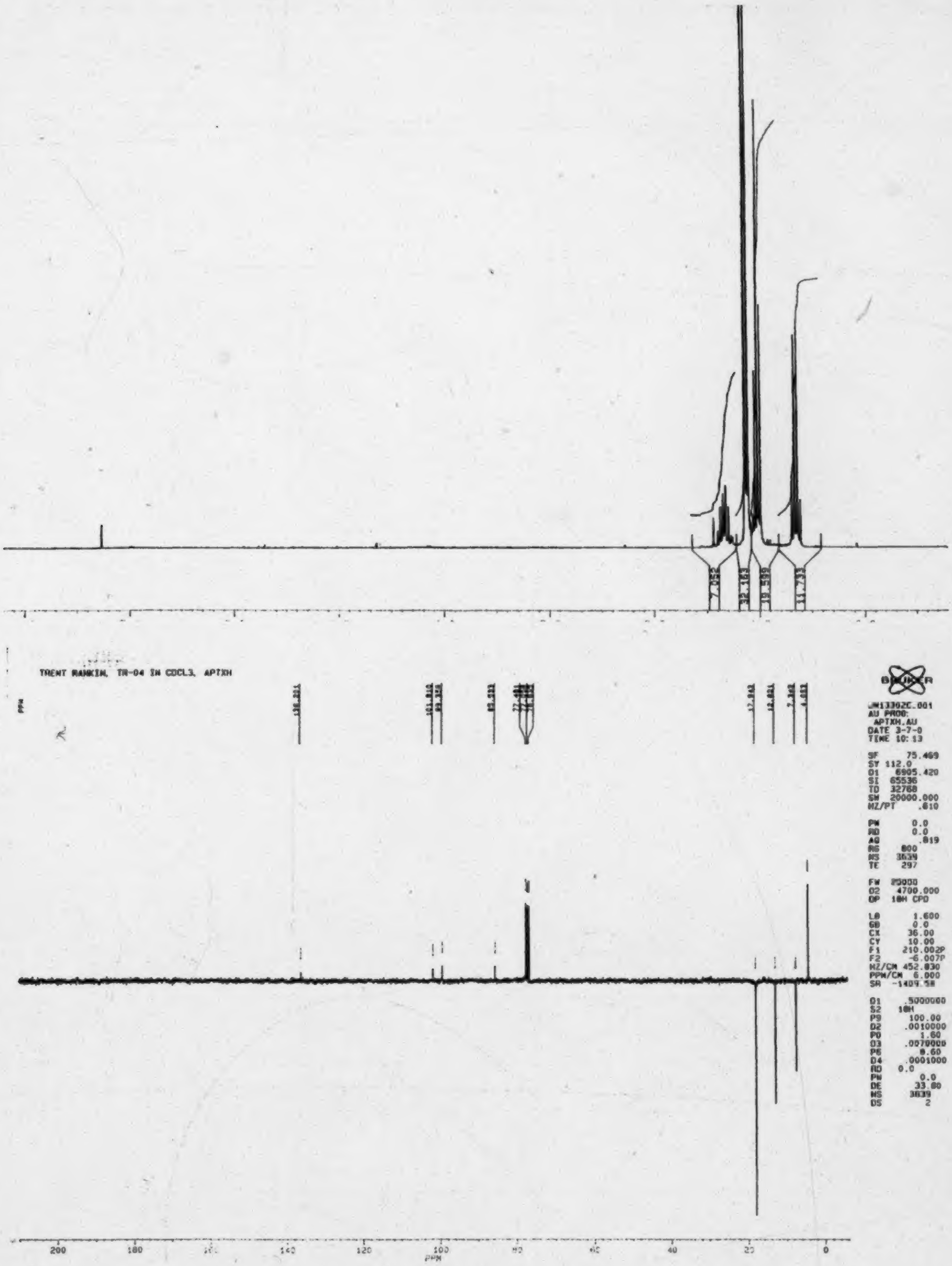
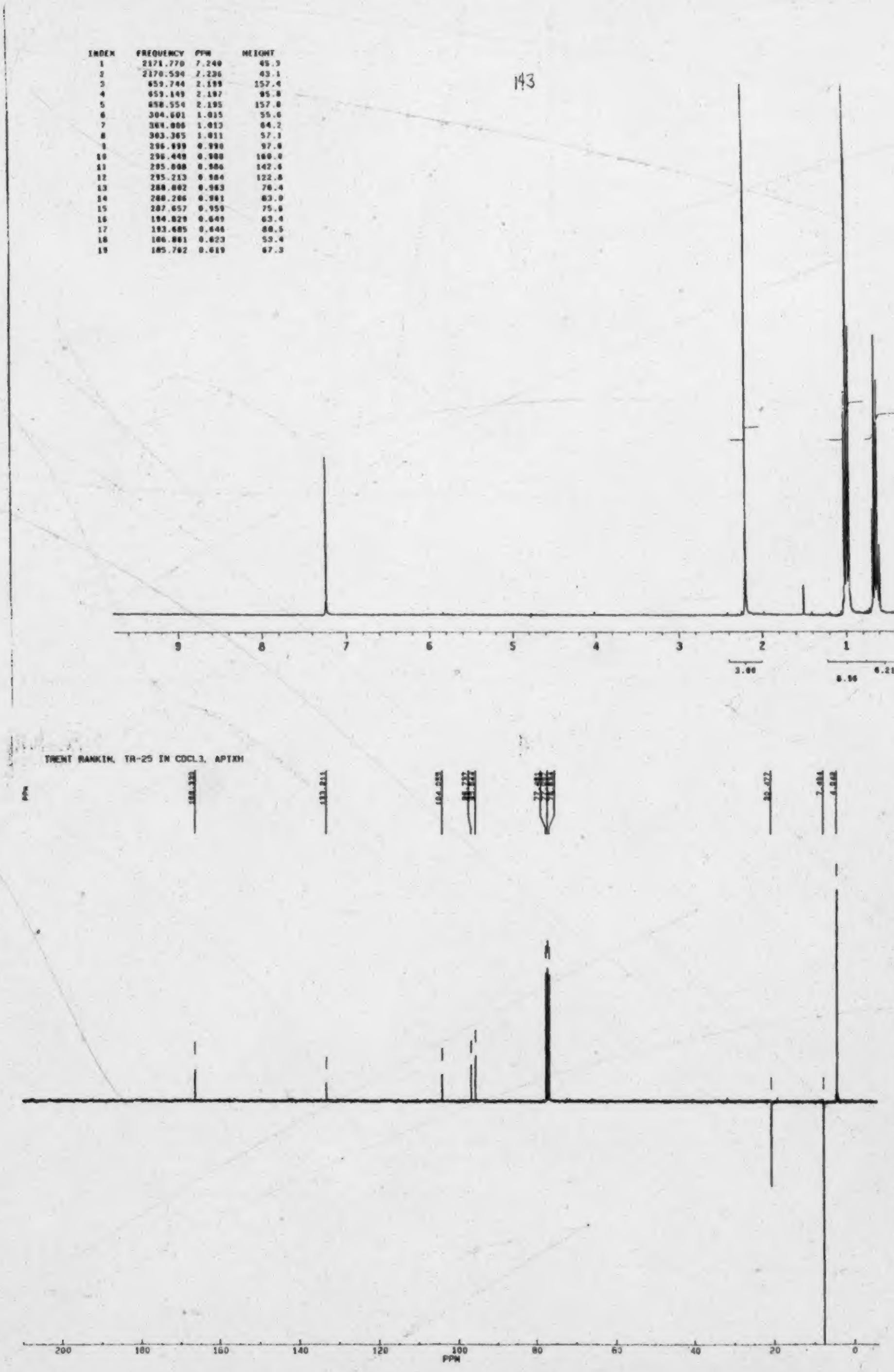


Figure 14. ^{1}H and ^{13}C NMR Spectra of Compound 5



INDEX	FREQUENCY	PPM	HEIGHT
1	2171.770	7.240	45.3
2	2170.594	7.236	43.1
3	659.744	2.199	157.4
4	659.149	2.197	95.8
5	658.554	2.195	157.0
6	304.601	1.015	55.6
7	304.006	1.013	64.2
8	303.365	1.011	57.1
9	296.999	0.990	97.0
10	296.449	0.988	160.0
11	295.808	0.986	142.6
12	295.213	0.984	122.8
13	288.802	0.963	76.4
14	288.206	0.961	83.0
15	287.657	0.959	75.6
16	194.829	0.649	63.4
17	193.685	0.646	80.5
18	186.881	0.623	53.4
19	185.702	0.619	67.3

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JA180F.103
AU PROG:
 X25 AU
DATE 7-5-1
TIME 11:41

SF      75.469
SY 112.0
O1    7000.000
SI   65536
TD   32768
SW   22727.273
HZ/PT      .694

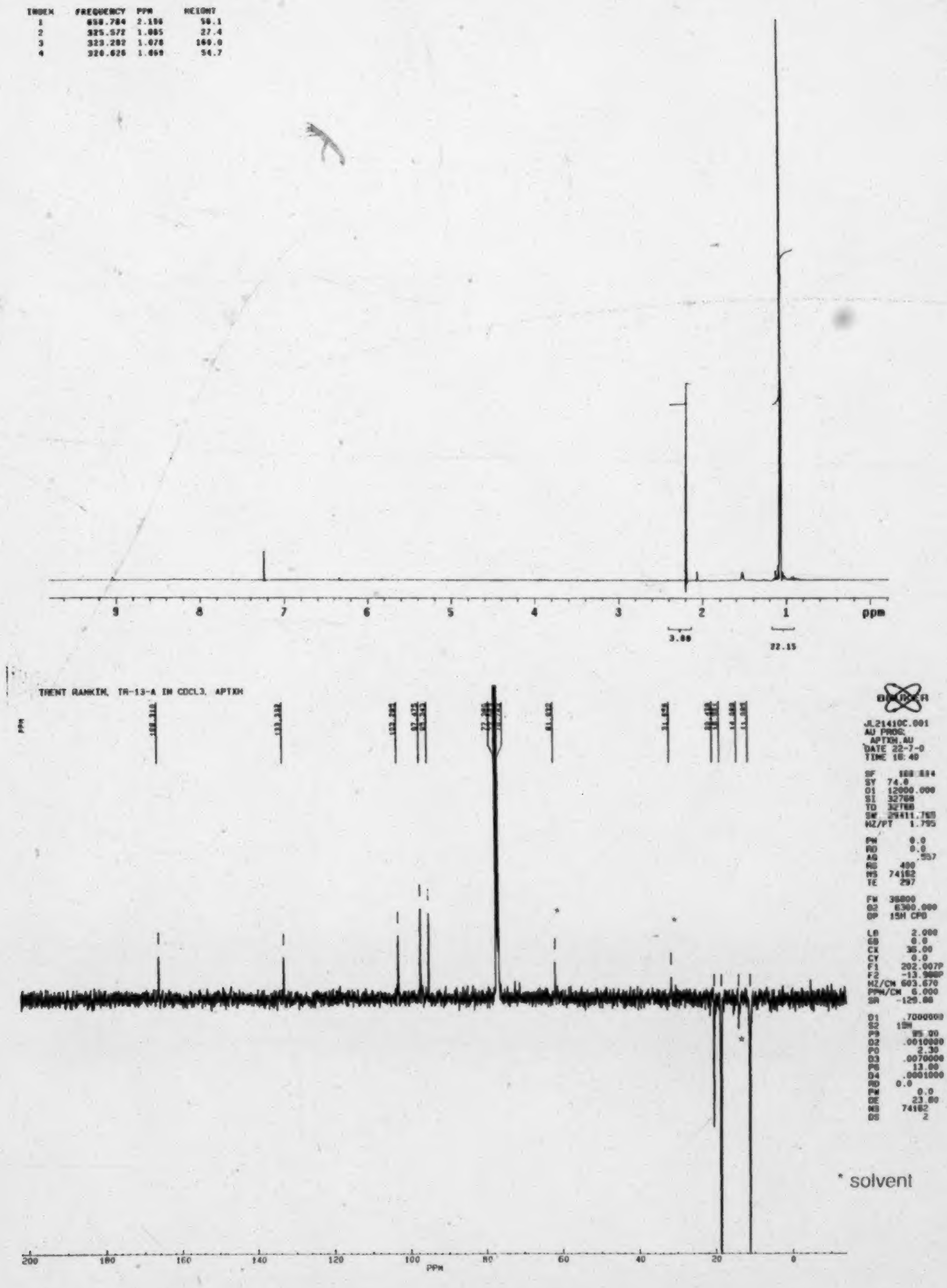
PW       0.0
RD       0.0
AQ        .721
RG     800
NS   27000
TE     297

FW   28500
O2    4425.000
DP   10H CPD

LB       1.000
GB        .010
CX      36.00
CY      10.00
F1     210.007P
F2      -5.993P
HZ/CM 452.812
PPM/CM  6.000
SR  -1409.60

D1      .5000000
S1    10H
P9      100.00
D2      .0010000
S2    10H
P0        1.60
D3      .0070000
P6        8.40
D4      .0001000
RGA
RD   0.0
PW        0.0
DE       30.00
NS     27000
DS         2
```

Figure 15. ^{1}H and ^{13}C NMR Spectra of Compound 6



INDEX	FREQUENCY	PPM	HEIGHT
1	658.784	2.196	58.1
2	325.572	1.085	27.4
3	323.202	1.078	100.0
4	320.626	1.069	54.7

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TD   32768
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HZ/PT    1.795

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RD        0.0
AQ         .557
RG       400
NS    74182
TE       297

FW   38000
O2     6300.000
DP   15H CPD

LB        2.000
GB        0.0
CX       36.00
CY        0.0
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F2      -13.988P
HZ/CM  603.670
PPM/CM   6.000
SR     -129.00

D1        .7000000
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P9        95.00
D2        .0010000
P0         2.30
D3        .0070000
P6        13.00
D4        .0001000
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NS      74182
DS          2
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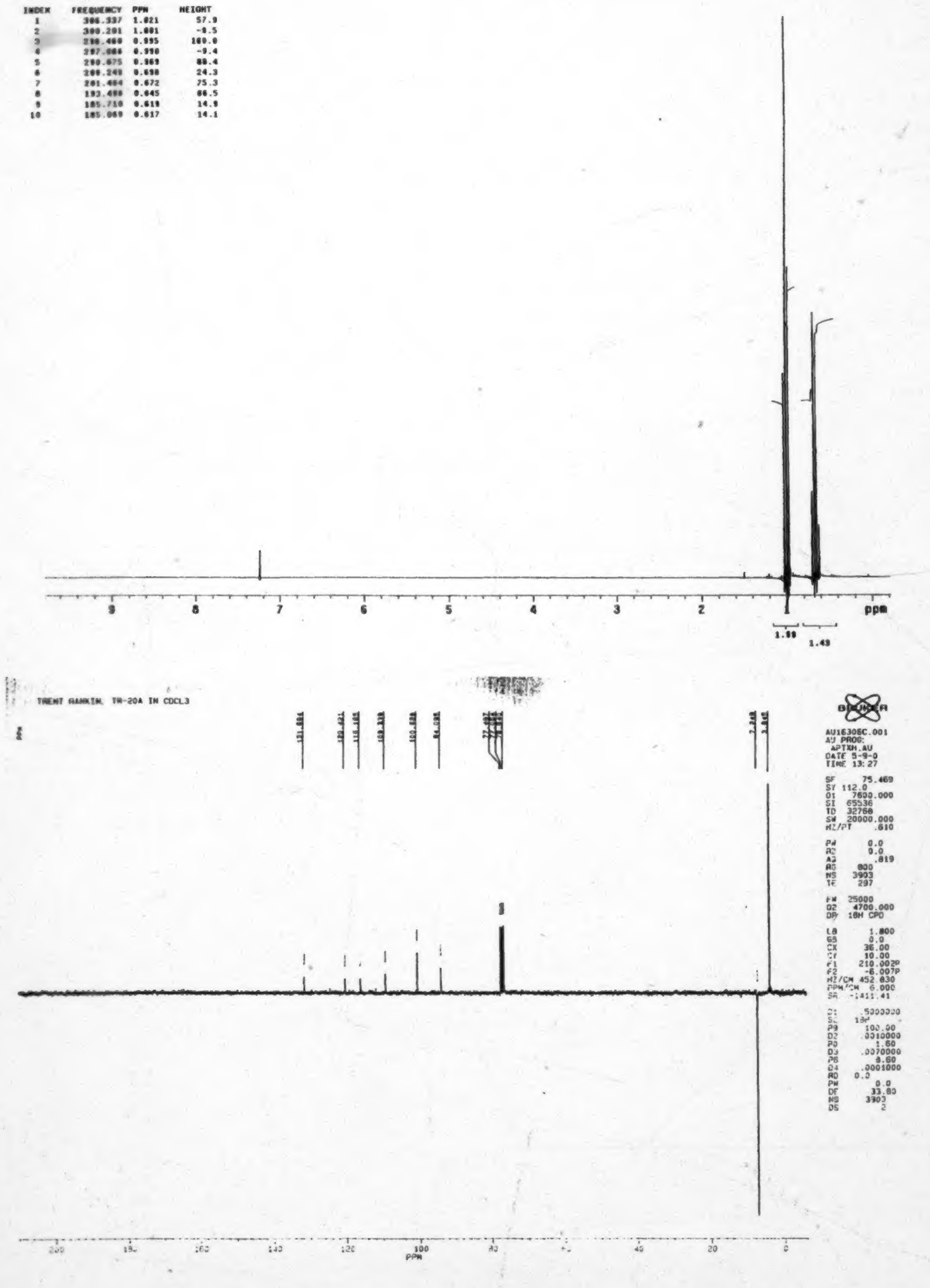
Figure 16. ^1H and ^{13}C NMR Spectra of Compound 7



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  1      306.337   1.021     57.9
  2      300.201   1.001     -8.5
  3      298.460   0.995    100.0
  4      297.086   0.990     -9.4
  5      290.675   0.969     88.4
  6      209.249   0.698     24.3
  7      201.464   0.672     75.3
  8      193.499   0.645     66.5
  9      185.710   0.619     14.9
 10      185.069   0.617     14.1
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TD   32768
SW   20000.000
HZ/PT     .610

PW       0.0
RD       0.0
AQ        .819
RG     800
NS    3903
TE     297

FW   25000
O2    4700.000
DP  18H CPD

LB       1.800
GB       0.0
CX      36.00
CY      10.00
F1     210.002P
F2      -6.007P
HZ/CM  452.830
PPM/CM   6.000
SR  -1411.41

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P9     100.00
D2      .0010000
P3       1.60
D3      .0070000
P6       8.60
D4      .0001000
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PW       0.0
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NS    3903
DS       2
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Figure 17. ¹H and ¹³C NMR Spectra of Compound 8

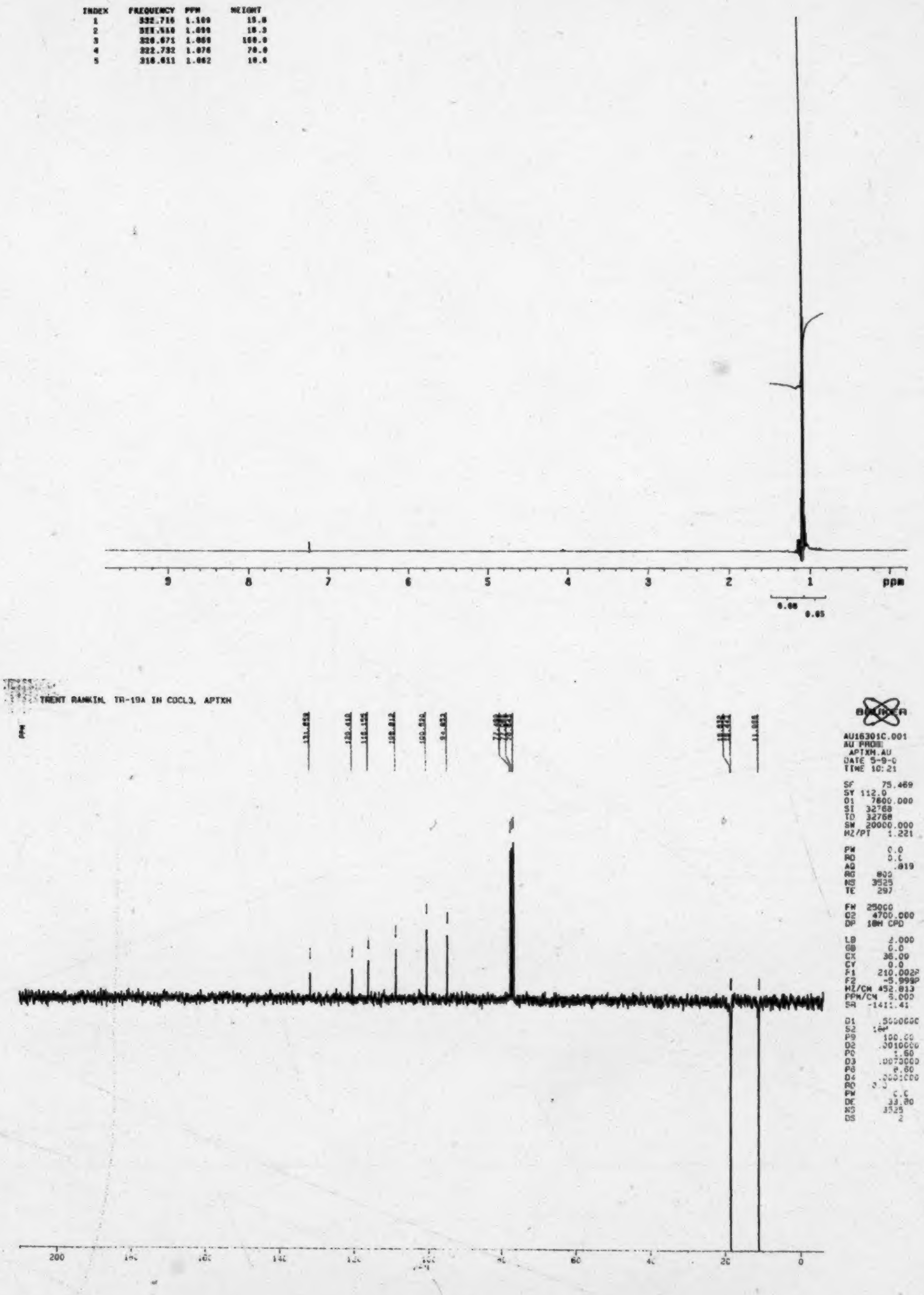
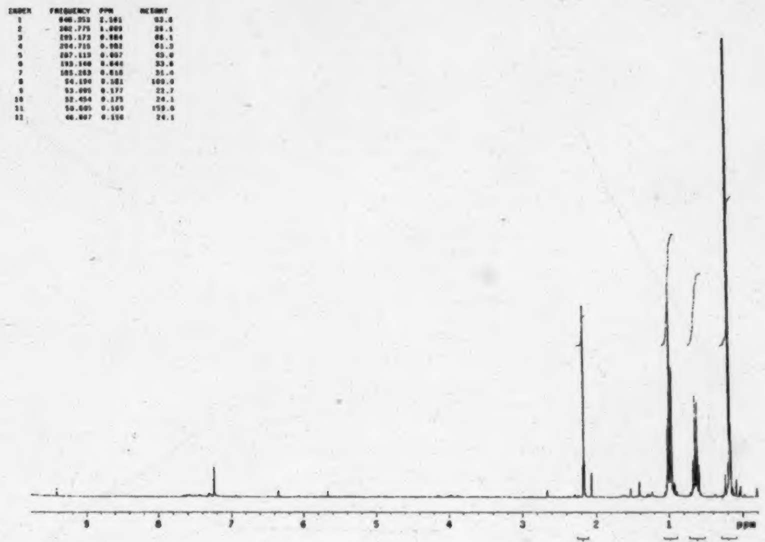


Figure 18. ^{1}H and ^{13}C NMR Spectra of Compound 9



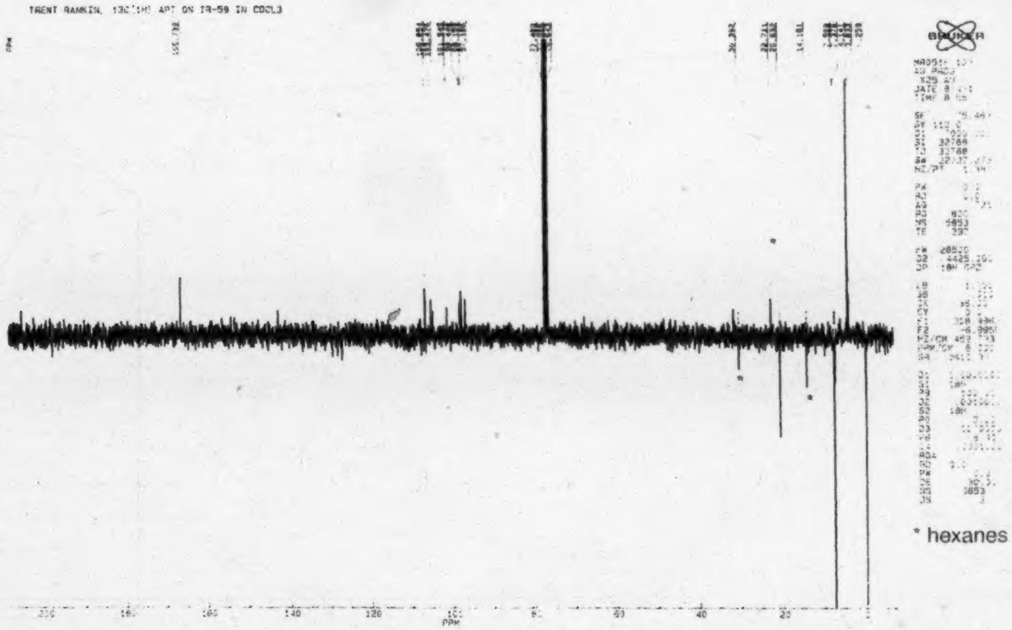


Figure 19. ^{1}H and ^{13}C NMR Spectra of Compound 10

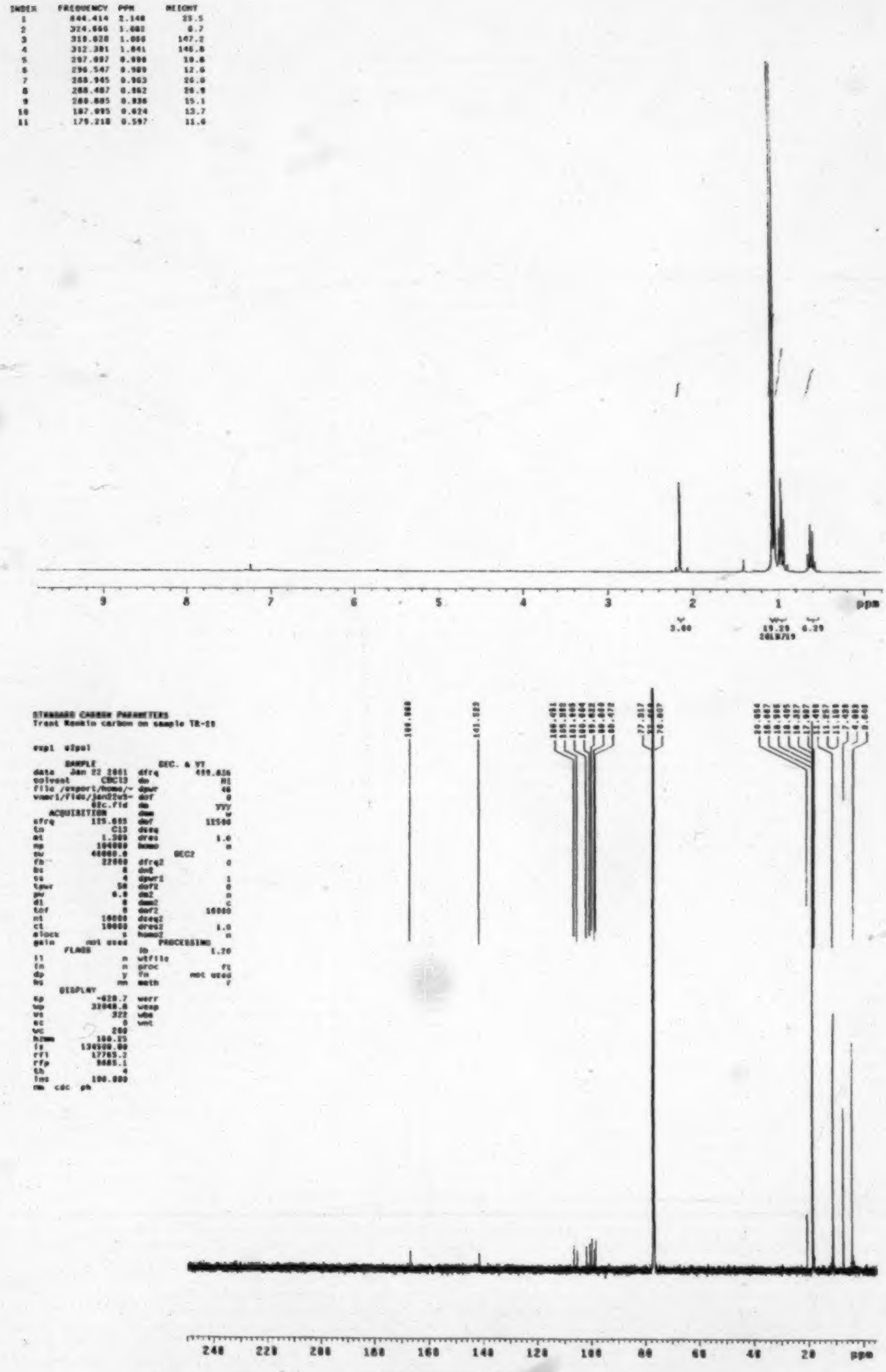
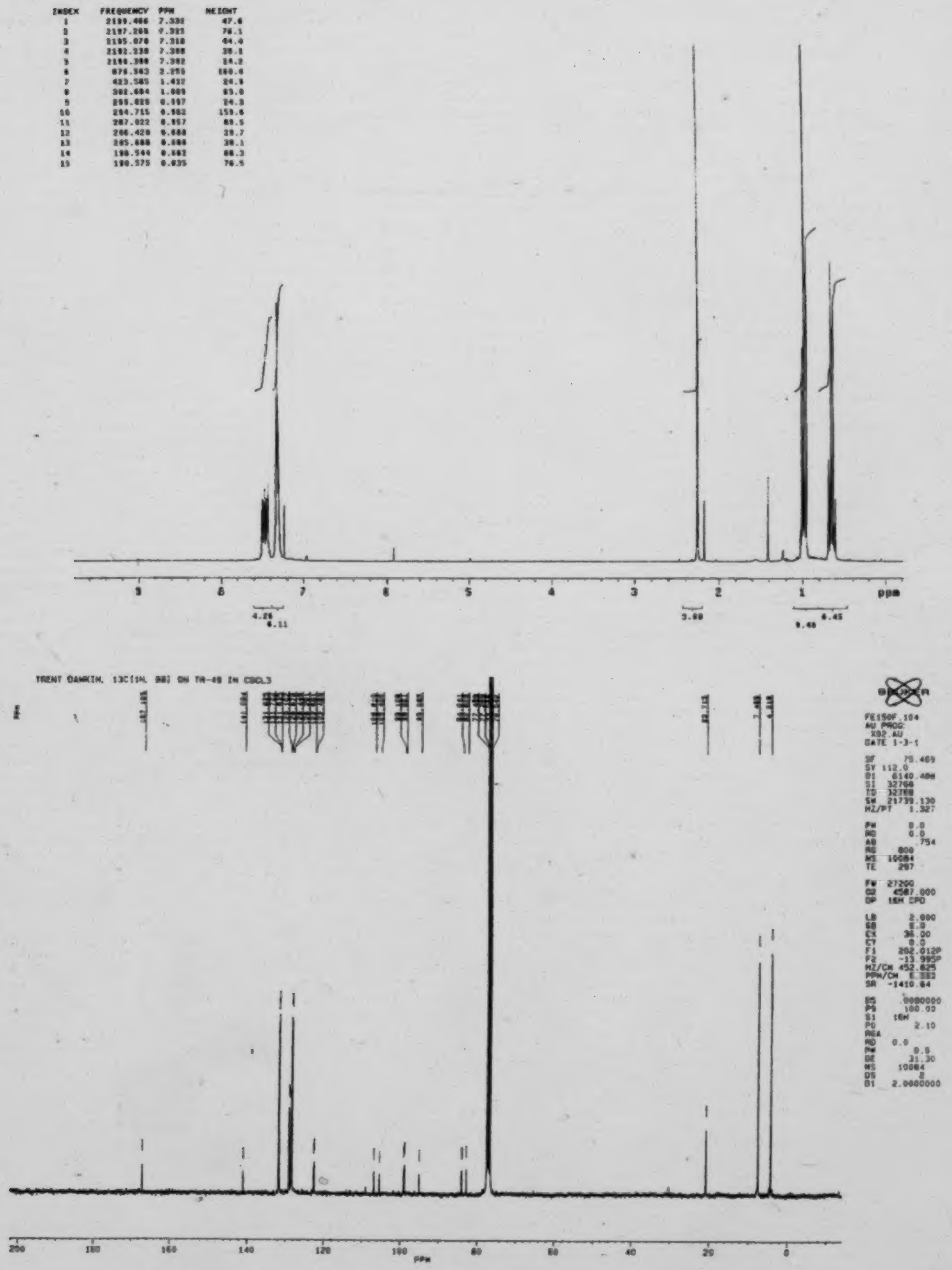


Figure 20. ¹H and ¹³C NMR Spectra of Compound 11



INDEX	FREQUENCY	PPM	HEIGHT
1	2199.466	7.332	47.6
2	2197.288	7.325	76.1
3	2195.070	7.318	64.4
4	2192.230	7.308	38.1
5	2190.390	7.302	14.2
6	676.563	2.255	160.0
7	423.585	1.412	24.9
8	302.684	1.009	63.0
9	299.020	0.997	24.3
10	294.715	0.982	155.6
11	287.022	0.957	89.5
12	206.420	0.688	28.7
13	205.688	0.686	38.1
14	198.544	0.662	88.3
15	190.575	0.635	76.5

Figure 21. ^{1}H and ^{13}C NMR Spectra of Compound 12

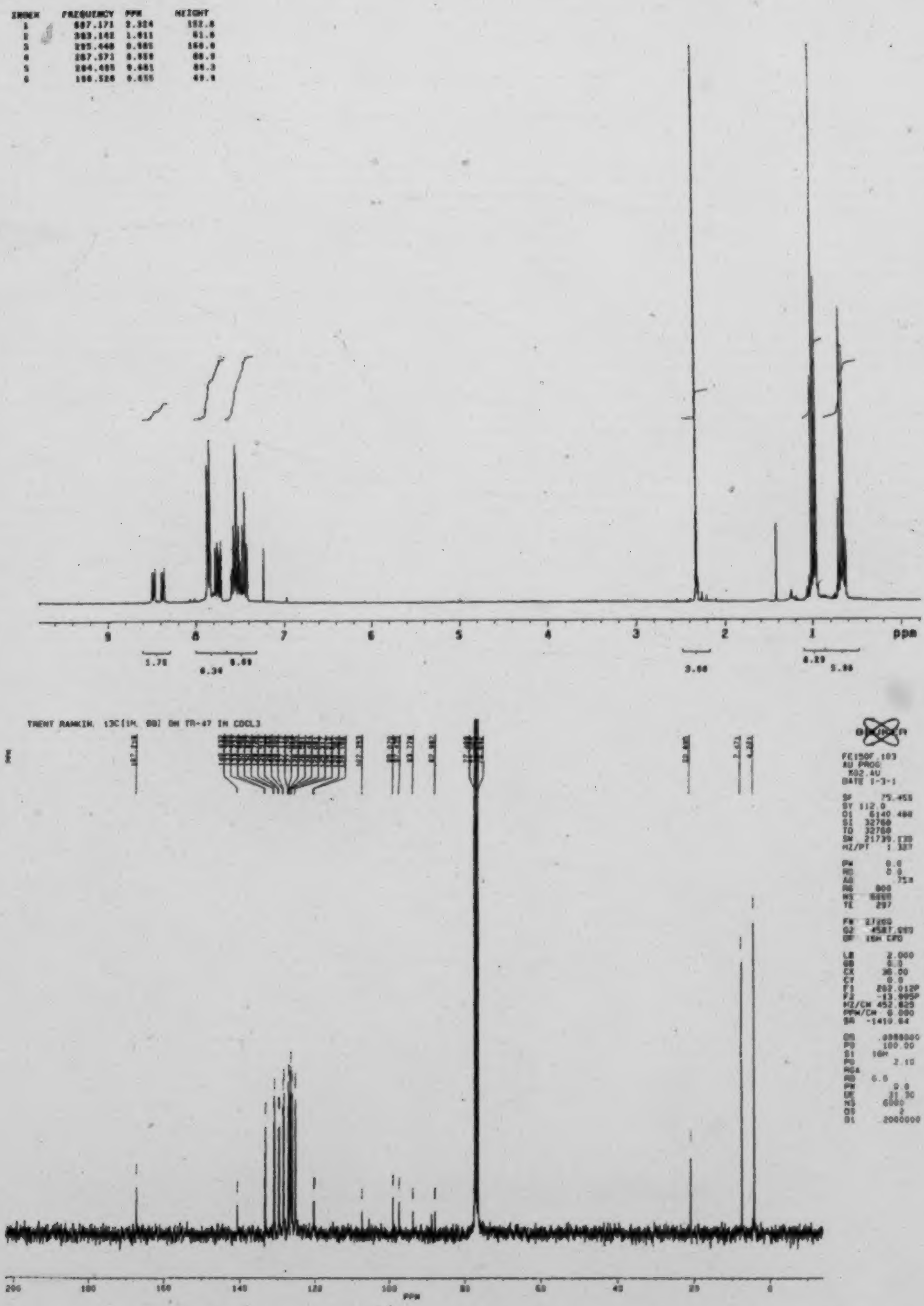


Figure 22. ^1H and ^{13}C NMR Spectra of Compound 13

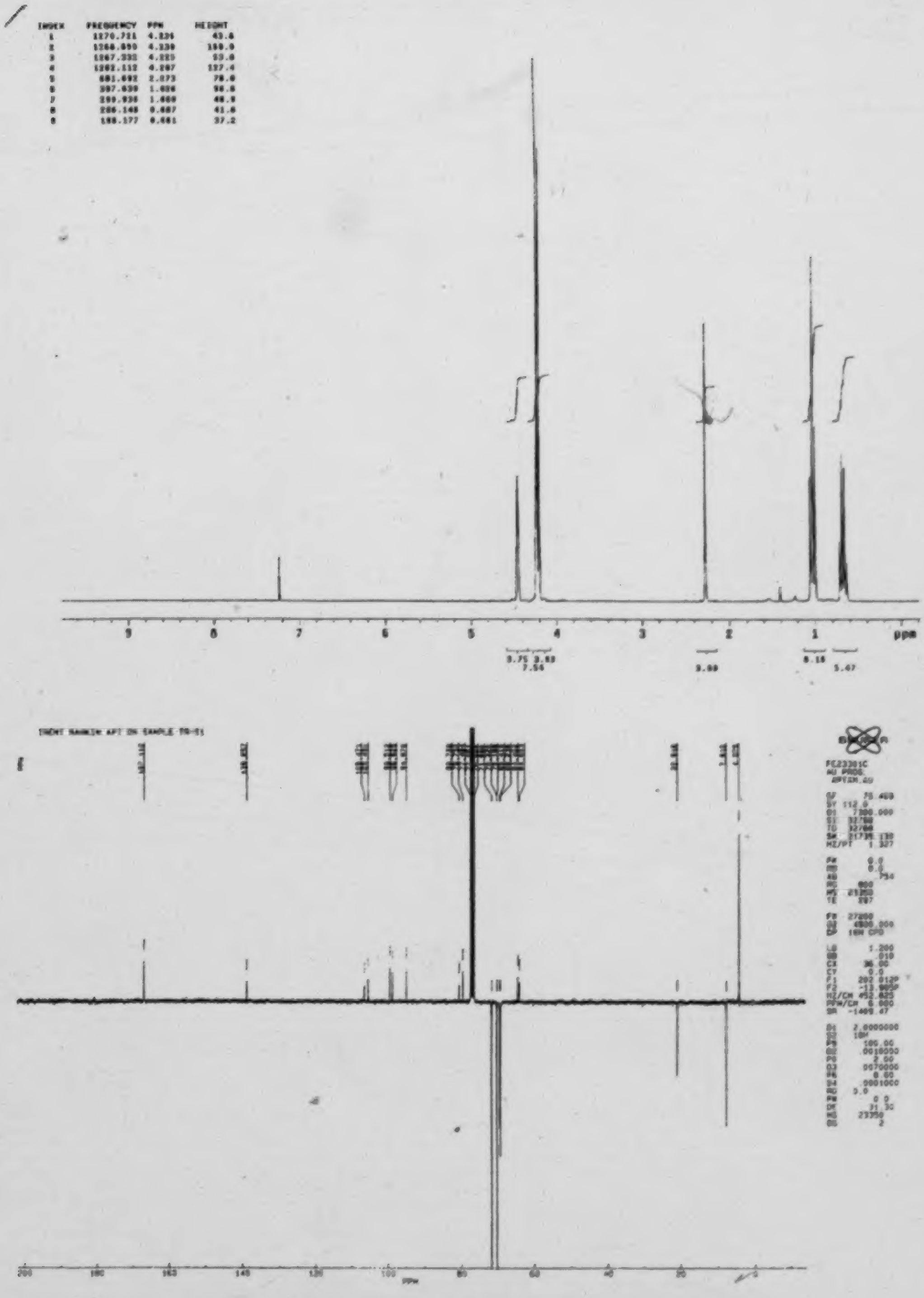
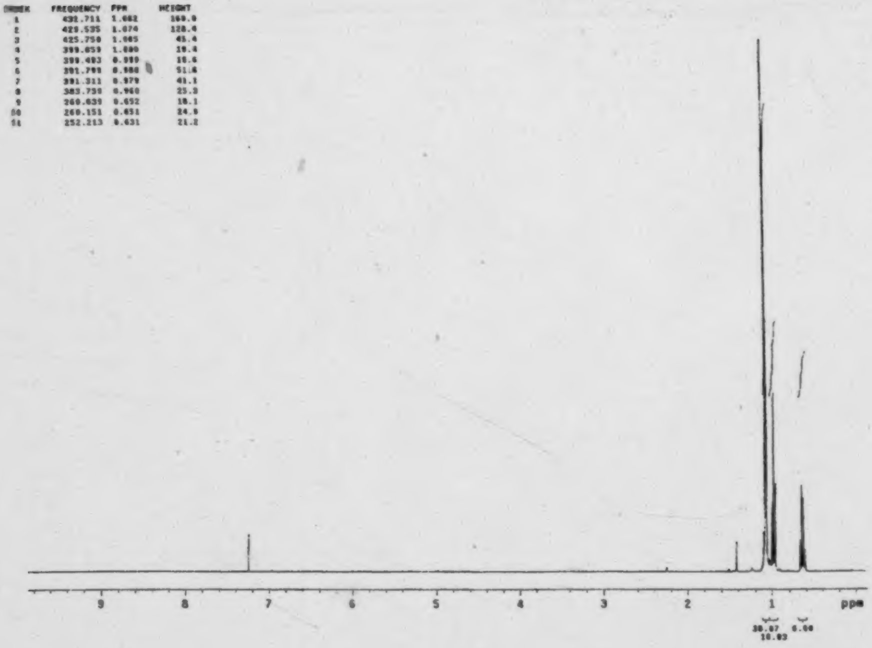


Figure 23. ^1H and ^{13}C NMR Spectra of Compound 14



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  1      432.711   1.082    160.0
  2      429.535   1.074    128.4
  3      425.750   1.065     45.4
  4      399.859   1.000     19.4
  5      399.483   0.999     18.6
  6      391.799   0.980     51.6
  7      391.311   0.979     41.1
  8      383.739   0.960     25.3
  9      260.839   0.652     18.1
 10      260.151   0.651     24.9
 11      252.213   0.631     21.2
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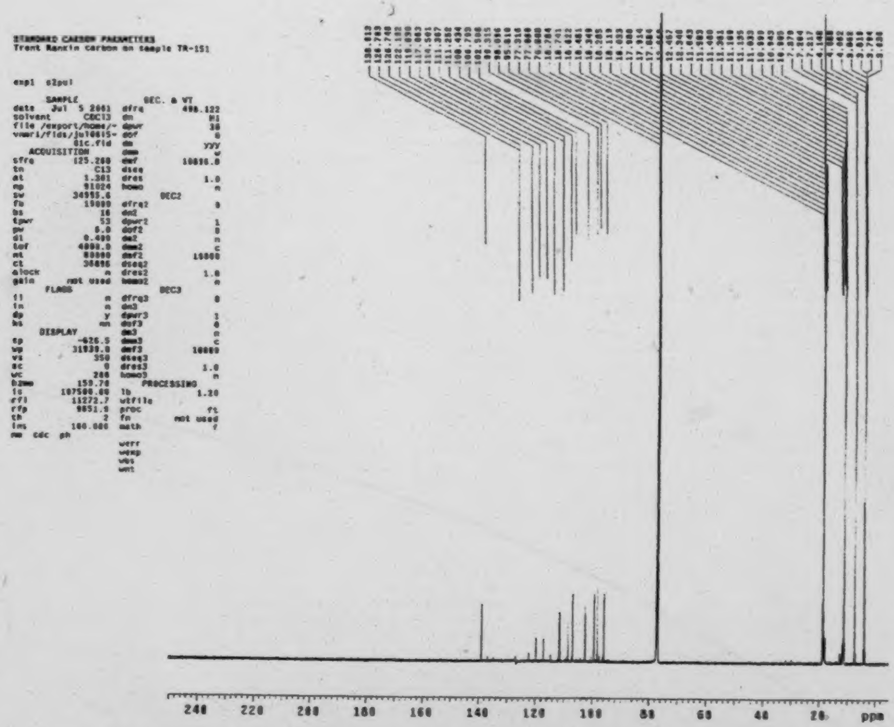

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tn             C13  dseq
at           1.301  dres              1.0
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sw         34995.6             DEC2
fb           19000  dfrq2               0
bs              16  dn2
tpwr            53  dpwr2               1
pw             6.0  dof2                0
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                    wnt
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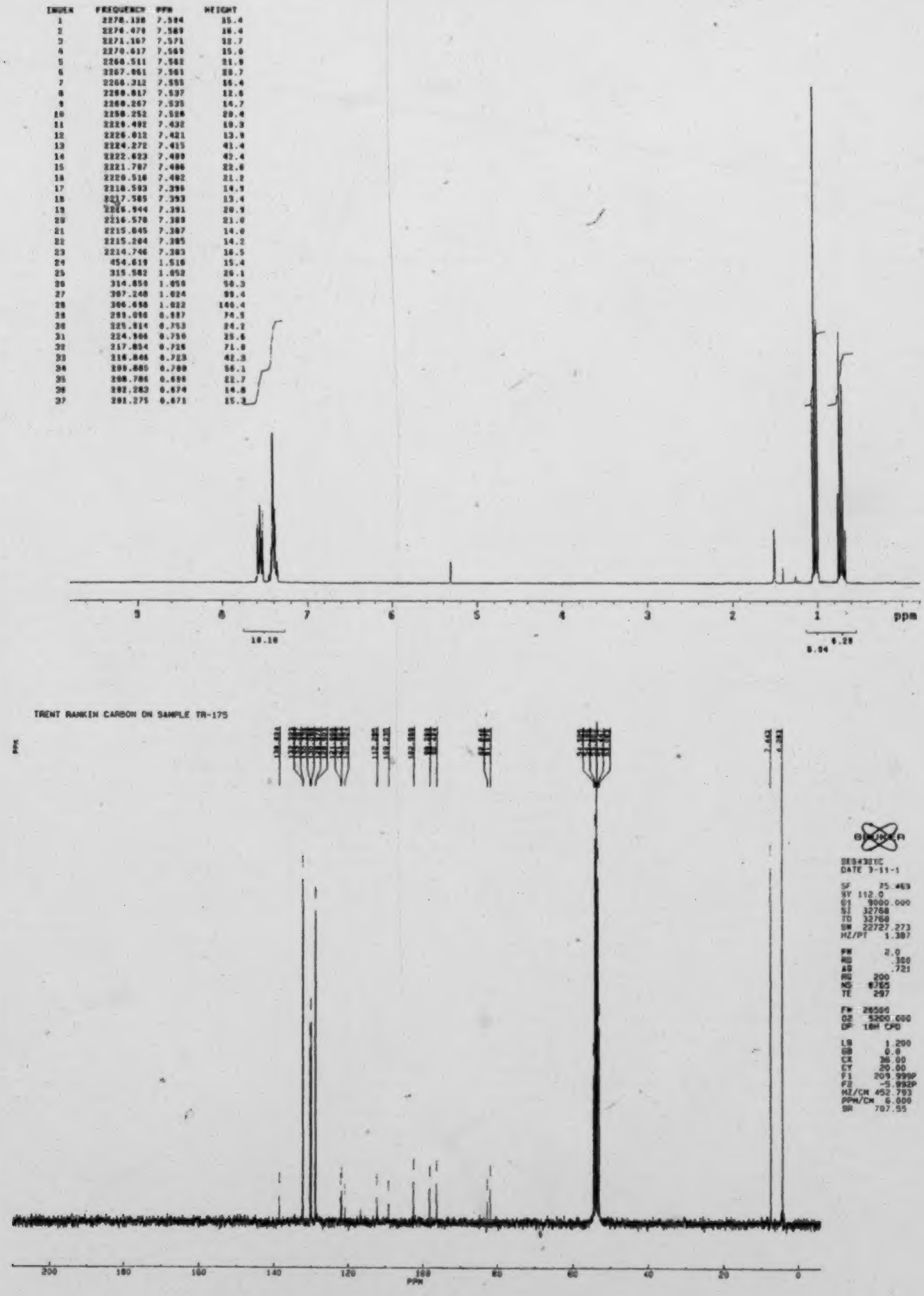
Figure 24. ¹H and ¹³C NMR Spectra of Compound 15



INDEX	FREQUENCY	PPM	HEIGHT
1	2278.128	7.594	15.4
2	2276.478	7.589	16.4
3	2271.167	7.571	12.7
4	2270.617	7.569	15.0
5	2268.511	7.562	21.9
6	2267.961	7.561	20.7
7	2266.312	7.555	16.4
8	2260.817	7.537	12.6
9	2260.267	7.535	14.7
10	2258.252	7.528	20.4
11	2229.492	7.432	10.3
12	2226.012	7.421	13.9
13	2224.272	7.415	41.4
14	2222.623	7.409	42.4
15	2221.707	7.406	22.6
16	2220.516	7.402	21.2
17	2218.593	7.396	14.9
18	2217.585	7.393	13.4
19	2216.944	7.391	20.9
20	2216.578	7.389	21.0
21	2215.845	7.387	14.0
22	2215.204	7.385	14.2
23	2214.746	7.383	16.5
24	454.619	1.516	15.4
25	315.582	1.052	26.1
26	314.850	1.050	50.3
27	307.248	1.024	89.4
28	306.698	1.022	140.4
29	293.096	0.977	74.5
30	225.914	0.753	24.2
31	224.906	0.750	25.6
32	217.854	0.726	71.0
33	216.846	0.723	42.3
34	209.885	0.700	56.1
35	208.786	0.696	22.7
36	202.283	0.674	14.8
37	201.275	0.671	15.3

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ppm
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9.04
6.29
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120
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80
60
40
20
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PPM
BRUKER

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DATE 3-11-1

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SI   32768
TD   32768
SW   22727.273
HZ/PT    1.387

PW         2.0
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AQ        .721
RG     200
NS    8765
TE     297

FW   28500
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LB       1.200
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CY      20.00
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PPM/CM   6.000
SR     707.55
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Figure 25. ^{1}H and ^{13}C NMR Spectra of Compound 16

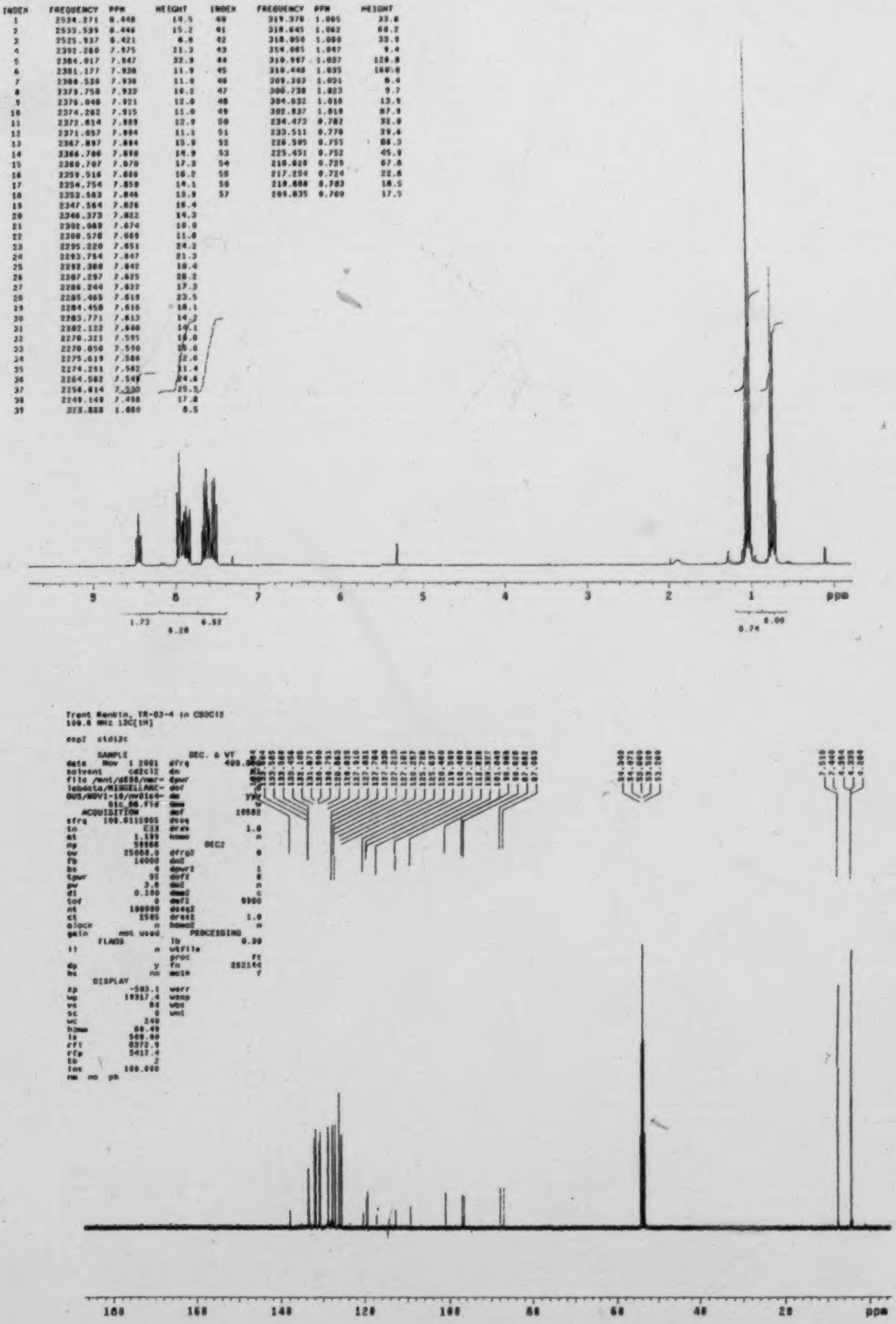
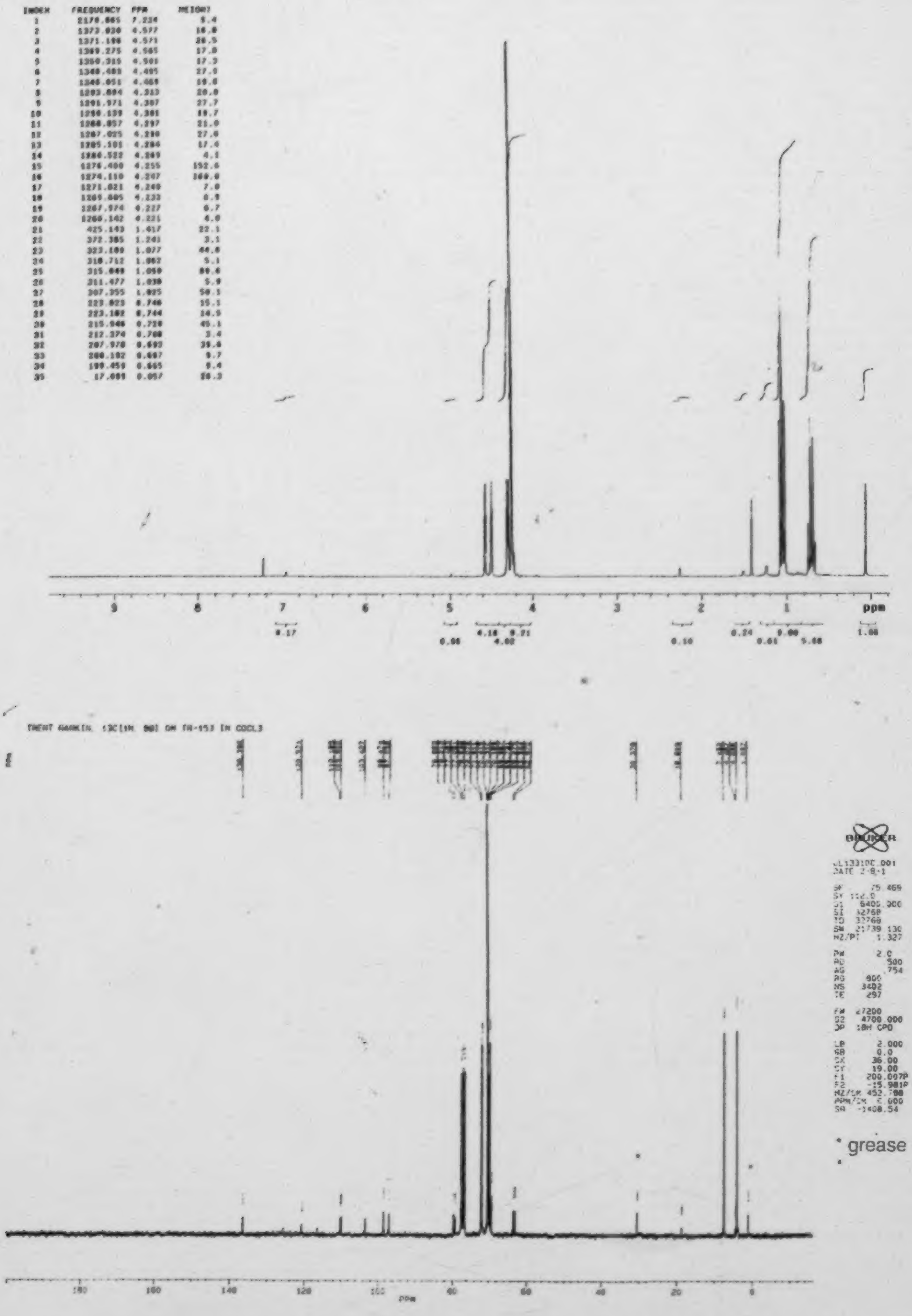


Figure 26. ^{1}H and ^{13}C NMR Spectra of Compound 17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INDEX     FREQUENCY  PPM       HEIGHT
  1        2170.065  7.234       5.4
  2        1373.030  4.577      16.8
  3        1371.198  4.571      26.5
  4        1369.275  4.565      17.8
  5        1350.315  4.501      17.3
  6        1348.483  4.495      27.0
  7        1346.651  4.489      16.6
  8        1293.894  4.313      20.0
  9        1291.971  4.307      27.7
 10        1290.139  4.301      18.7
 11        1288.857  4.297      21.0
 12        1287.025  4.290      27.6
 13        1285.101  4.284      17.4
 14        1280.522  4.269       4.1
 15        1276.400  4.255     152.6
 16        1274.110  4.247     160.0
 17        1271.821  4.240       7.0
 18        1269.805  4.233       6.9
 19        1267.974  4.227       6.7
 20        1266.142  4.221       4.0
 21         425.143  1.417      22.1
 22         372.385  1.241       3.1
 23         323.189  1.077      44.8
 24         318.712  1.062       5.1
 25         315.040  1.050      89.6
 26         311.477  1.038       5.9
 27         307.355  1.025      50.1
 28         223.823  0.746      15.1
 29         223.182  0.744      14.5
 30         215.946  0.720      45.1
 31         212.374  0.708       3.4
 32         207.978  0.693      35.6
 33         200.102  0.667       9.7
 34         199.459  0.665       8.4
 35          17.089  0.057      26.3
```
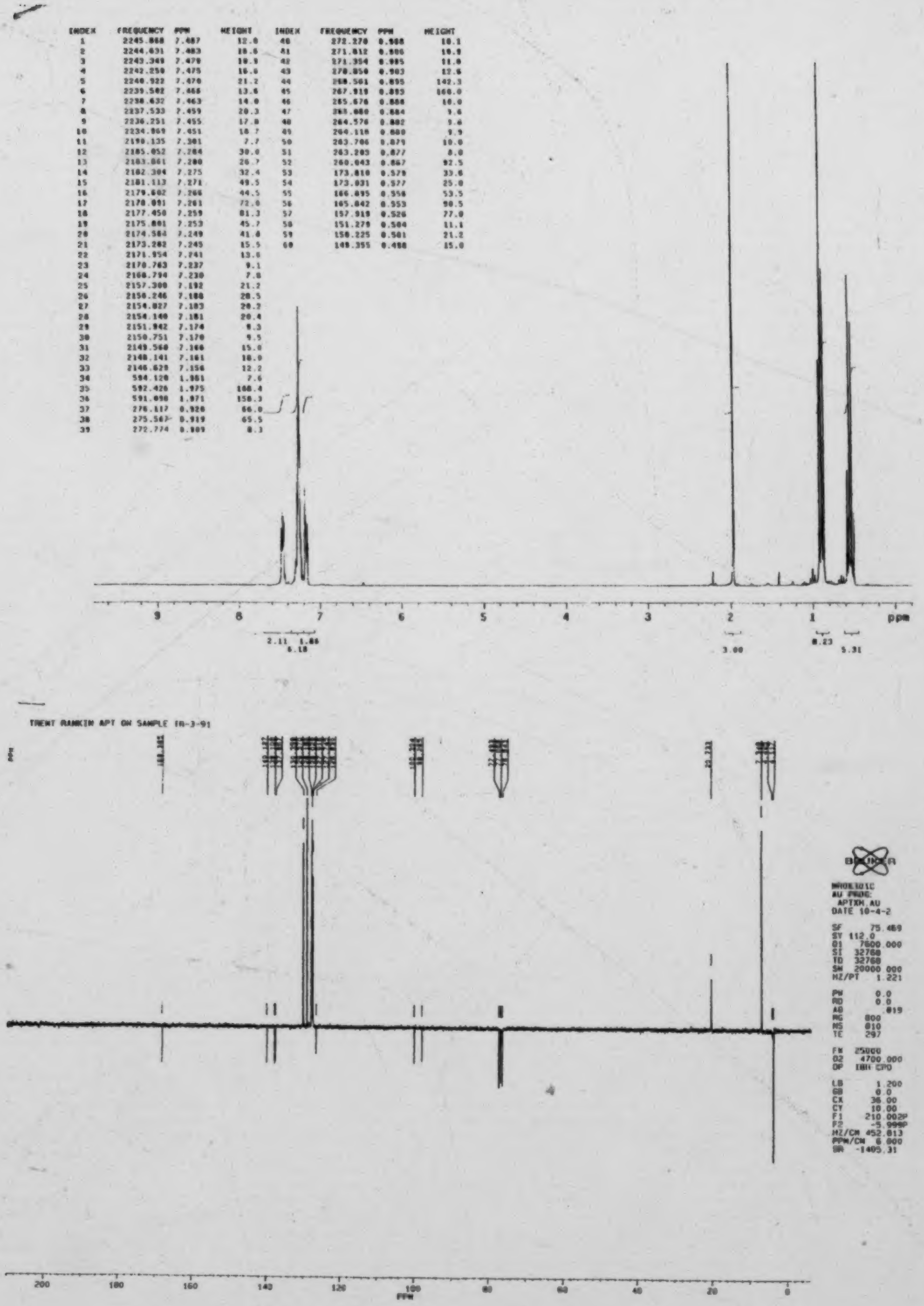

TRENT HANKIN 13C(1H 90) ON TH-153 IN CDCL3

```
JL13310C.001
DATE 2-8-1

SF       75.469
SY   112.0
O1     6400.000
SI    32768
TD    32768
SW    21739.130
HZ/PT     1.327

PW        2.0
RD         .500
AQ         .754
RG      800
NS     3402
TE      297

FW    27200
O2     4700.000
DP   10H CPD

LB        2.000
GB        0.0
CX       36.00
CY       19.00
F1      200.007P
F2      -15.981P
HZ/CM   452.708
PPM/CM    6.000
SR    -1408.54
```

* grease

Figure 27. ^{1}H and ^{13}C NMR Spectra of Compound 18



INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	2245.868	7.487	12.0	40	272.270	0.908	10.1
2	2244.631	7.483	10.6	41	271.812	0.906	10.9
3	2243.349	7.479	10.9	42	271.354	0.905	11.0
4	2242.250	7.475	16.6	43	270.850	0.903	12.6
5	2240.922	7.470	21.2	44	268.561	0.895	142.3
6	2239.502	7.466	13.6	45	267.919	0.893	160.0
7	2238.632	7.463	14.0	46	265.676	0.886	10.0
8	2237.533	7.459	20.3	47	265.080	0.884	9.6
9	2236.251	7.455	17.0	48	264.576	0.882	9.6
10	2234.969	7.451	18.7	49	264.118	0.880	9.9
11	2190.135	7.301	7.7	50	263.706	0.879	10.0
12	2185.052	7.284	30.0	51	263.203	0.877	8.0
13	2183.861	7.280	26.7	52	260.043	0.867	92.5
14	2182.304	7.275	32.4	53	173.810	0.579	33.6
15	2181.113	7.271	49.5	54	173.031	0.577	25.0
16	2179.602	7.266	44.5	55	166.895	0.556	53.5
17	2178.091	7.261	72.0	56	165.842	0.553	90.5
18	2177.450	7.259	81.3	57	157.919	0.526	77.0
19	2175.801	7.253	45.7	58	151.279	0.504	11.1
20	2174.564	7.249	41.8	59	150.225	0.501	21.2
21	2173.282	7.245	15.5	60	146.355	0.488	15.0
22	2171.954	7.241	13.6				
23	2170.763	7.237	9.1				
24	2168.794	7.230	7.8				
25	2157.300	7.192	21.2				
26	2156.246	7.188	20.5				
27	2154.827	7.183	20.2				
28	2154.140	7.181	20.4				
29	2151.942	7.174	9.3				
30	2150.751	7.170	9.5				
31	2149.560	7.166	15.0				
32	2148.141	7.161	18.0				
33	2146.629	7.156	12.2				
34	594.120	1.981	7.6				
35	592.426	1.975	108.4				
36	591.098	1.971	158.3				
37	276.117	0.920	66.0				
38	275.567	0.919	65.5				
39	272.774	0.909	8.3				

```
MRO81011C
AU PROG:
 APTXH.AU
DATE 10-4-2

SF      75.469
SY  112.0
O1     7600.000
SI   32768
TD   32768
SW   20000.000
HZ/PT     1.221

PW        0.0
RD        0.0
AQ         .819
RG      800
NS      810
TE      297

FW   25000
O2     4700.000
DP   18H CPD

LB        1.200
GB        0.0
CX       36.00
CY       10.00
F1      210.002P
F2       -5.999P
HZ/CM  452.813
PPM/CM   6.000
SR   -1405.31
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Figure 28. ^{1}H and ^{13}C NMR Spectra of Compound 19

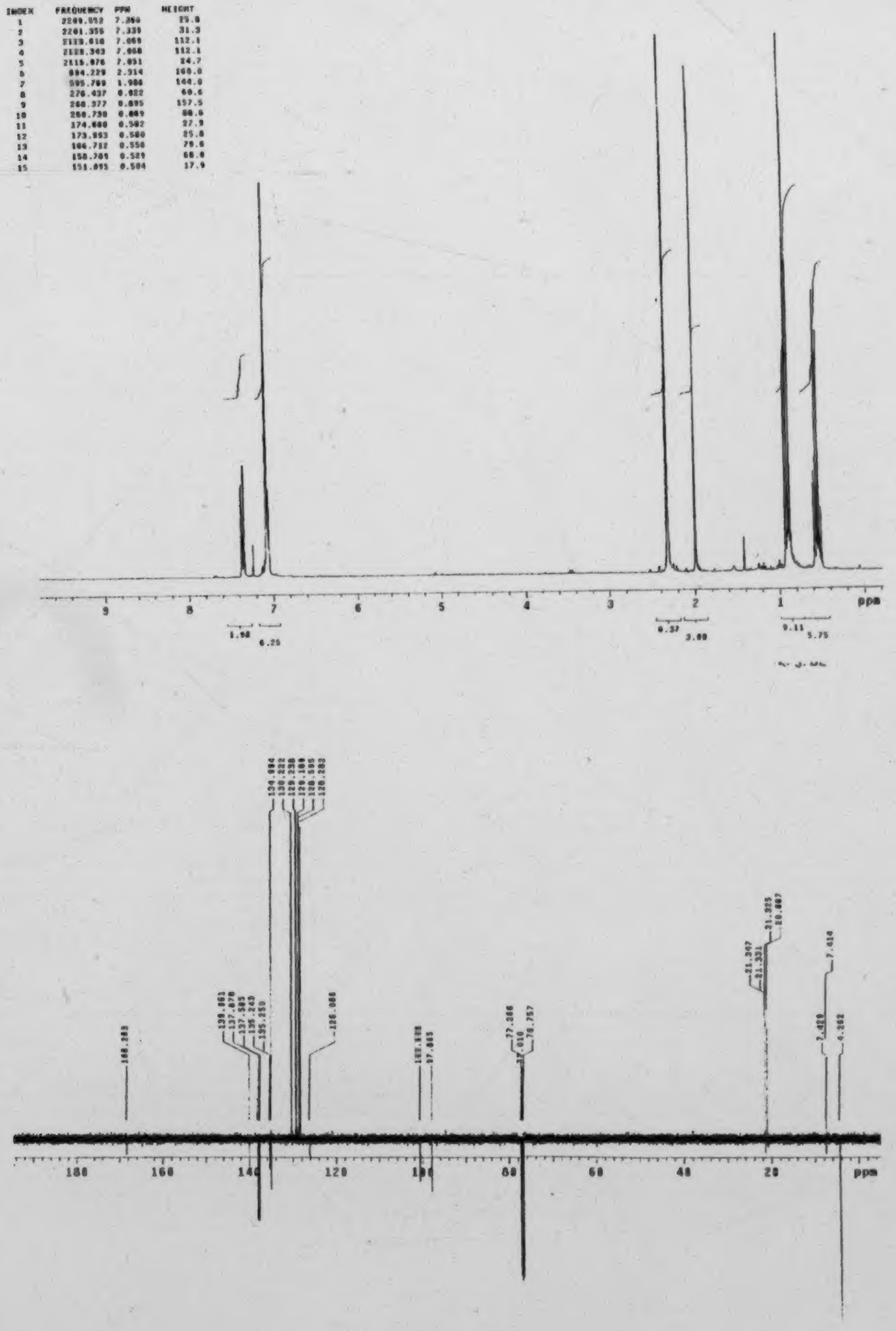
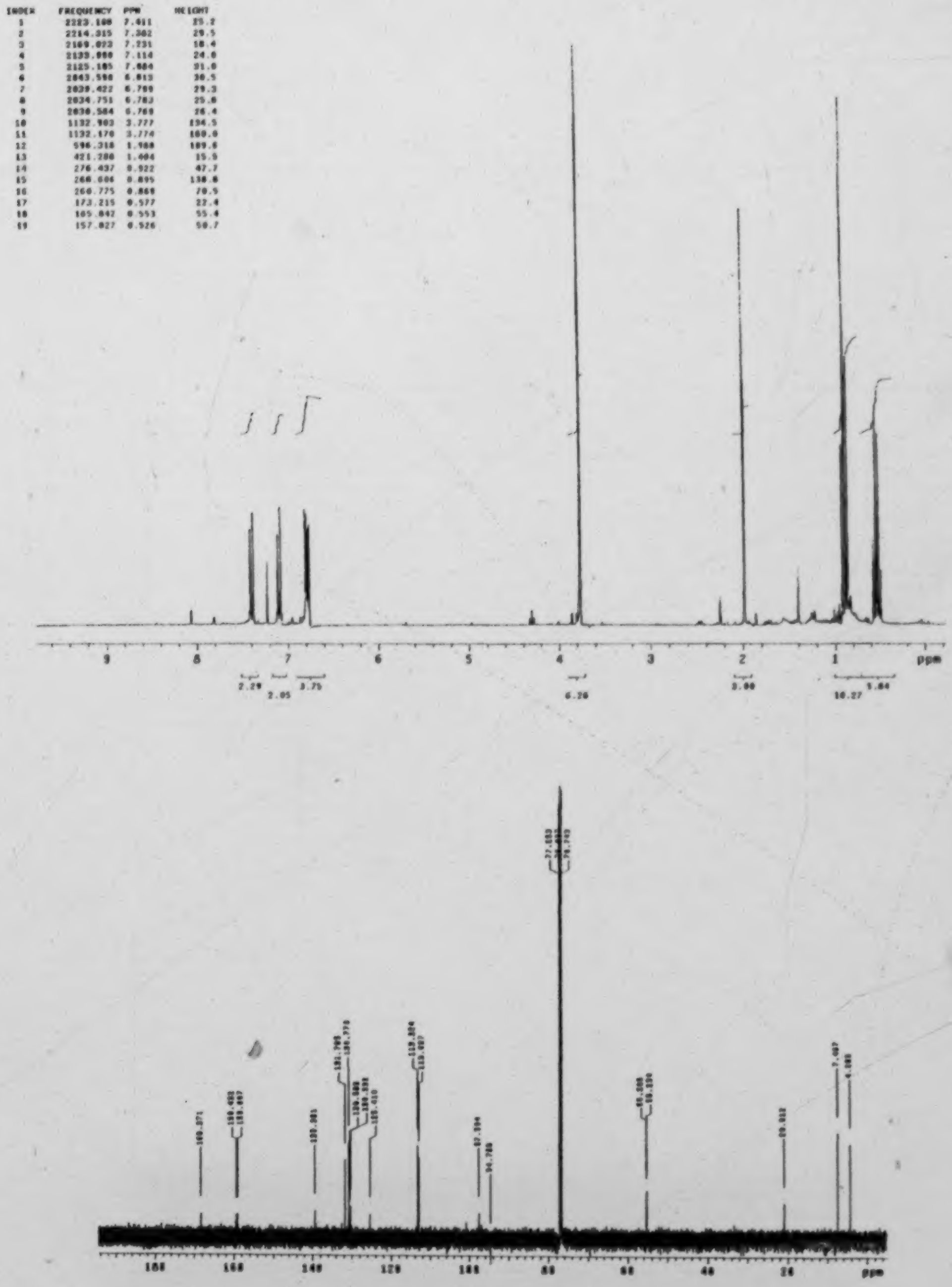


Figure 29. ^{1}H and ^{13}C NMR Spectra of Compound 20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INDEX    FREQUENCY  PPM      HEIGHT
  1       2223.100  7.411      25.2
  2       2214.315  7.382      29.5
  3       2169.072  7.231      18.4
  4       2133.990  7.114      24.0
  5       2125.185  7.084      31.0
  6       2043.598  6.813      30.5
  7       2039.422  6.799      29.3
  8       2034.751  6.783      25.0
  9       2030.584  6.769      26.4
 10       1132.903  3.777     134.5
 11       1132.170  3.774     160.0
 12        596.318  1.988     109.0
 13        421.200  1.404      15.5
 14        276.437  0.922      47.7
 15        268.606  0.895     130.0
 16        260.775  0.869      70.5
 17        173.215  0.577      22.4
 18        165.842  0.553      55.4
 19        157.827  0.526      50.7
```
9
8
7
6
5
4
3
2
1
ppm
2.29
2.05
3.75
6.26
3.00
10.27
5.84
169.371
159.492
159.467
139.301
131.795
130.770
130.508
130.336
126.410
114.504
114.497
97.394
94.780
77.423
77.000
76.577
55.308
55.250
20.912
7.497
4.083
180
160
140
120
100
80
60
40
20
ppm

Figure 30. ^{1}H and ^{13}C NMR Spectra of Compound 21

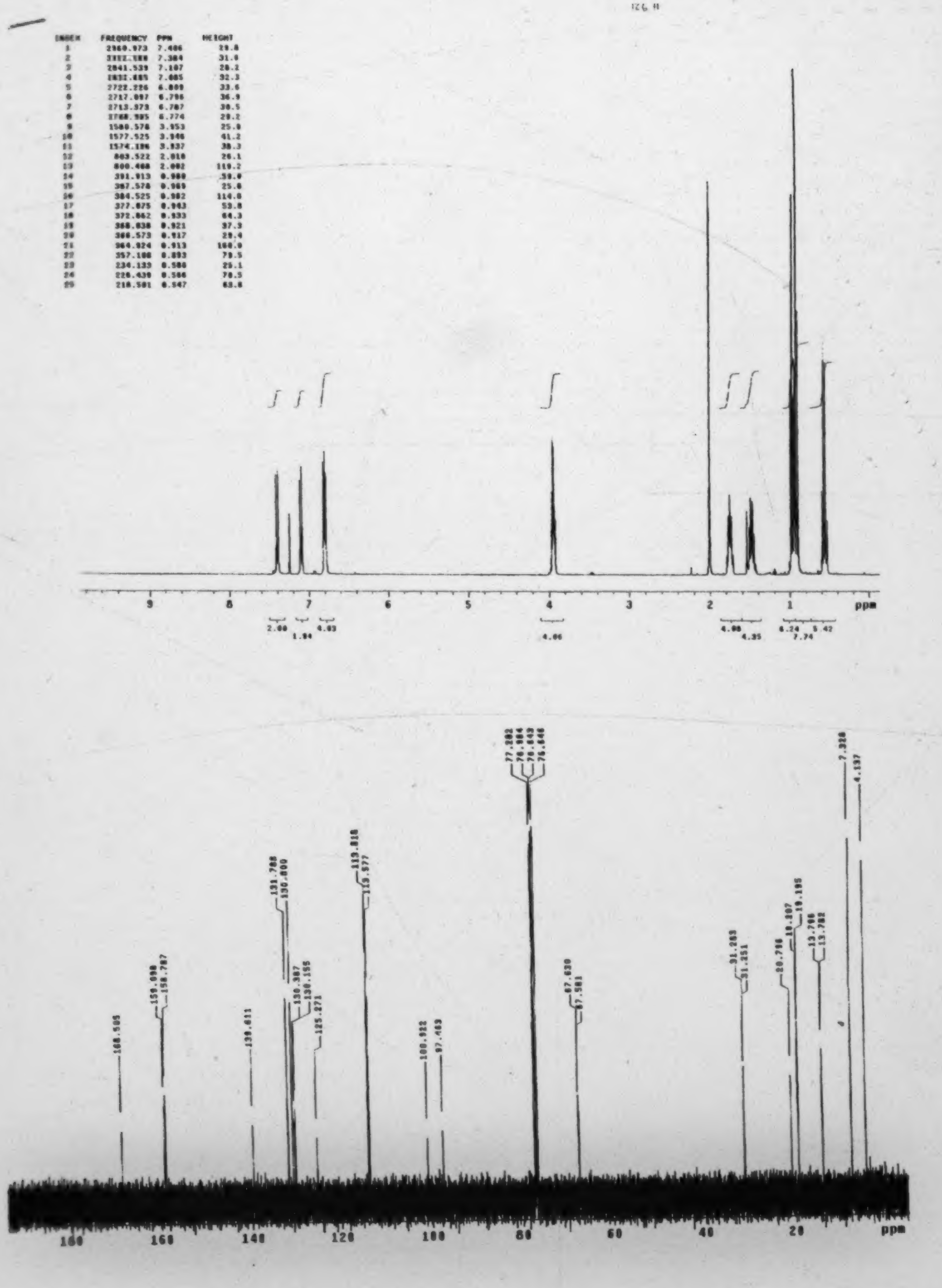
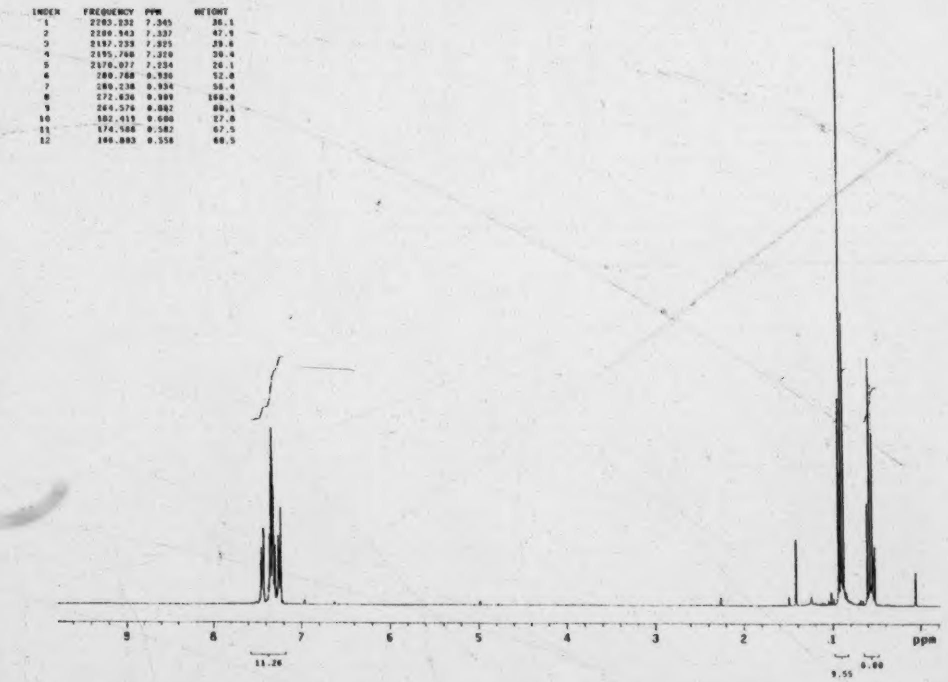
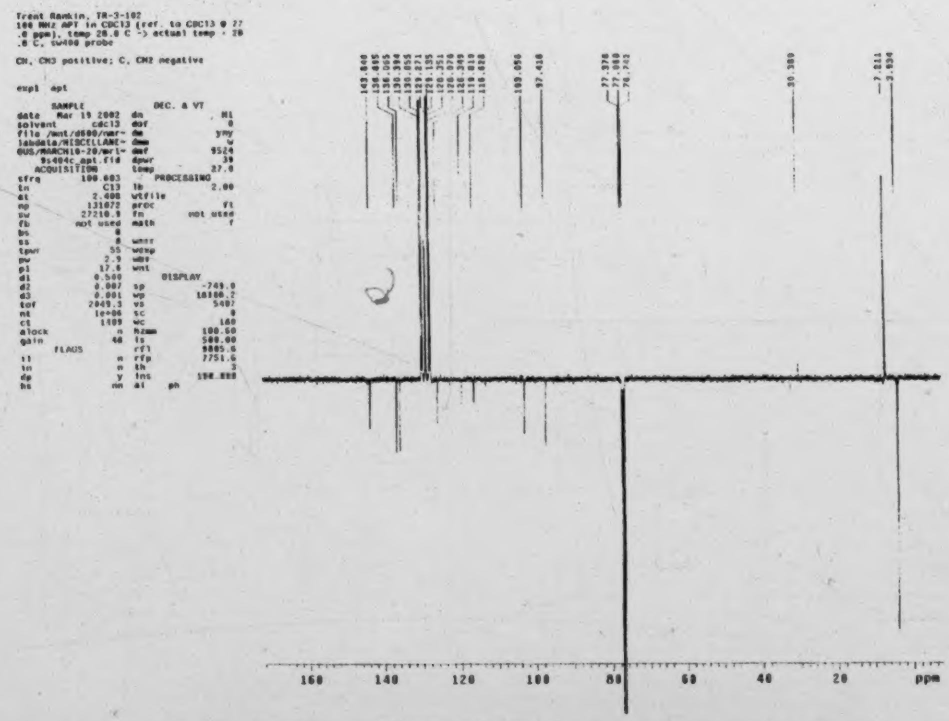


Figure 31. ^{1}H and ^{13}C NMR Spectra of Compound 22



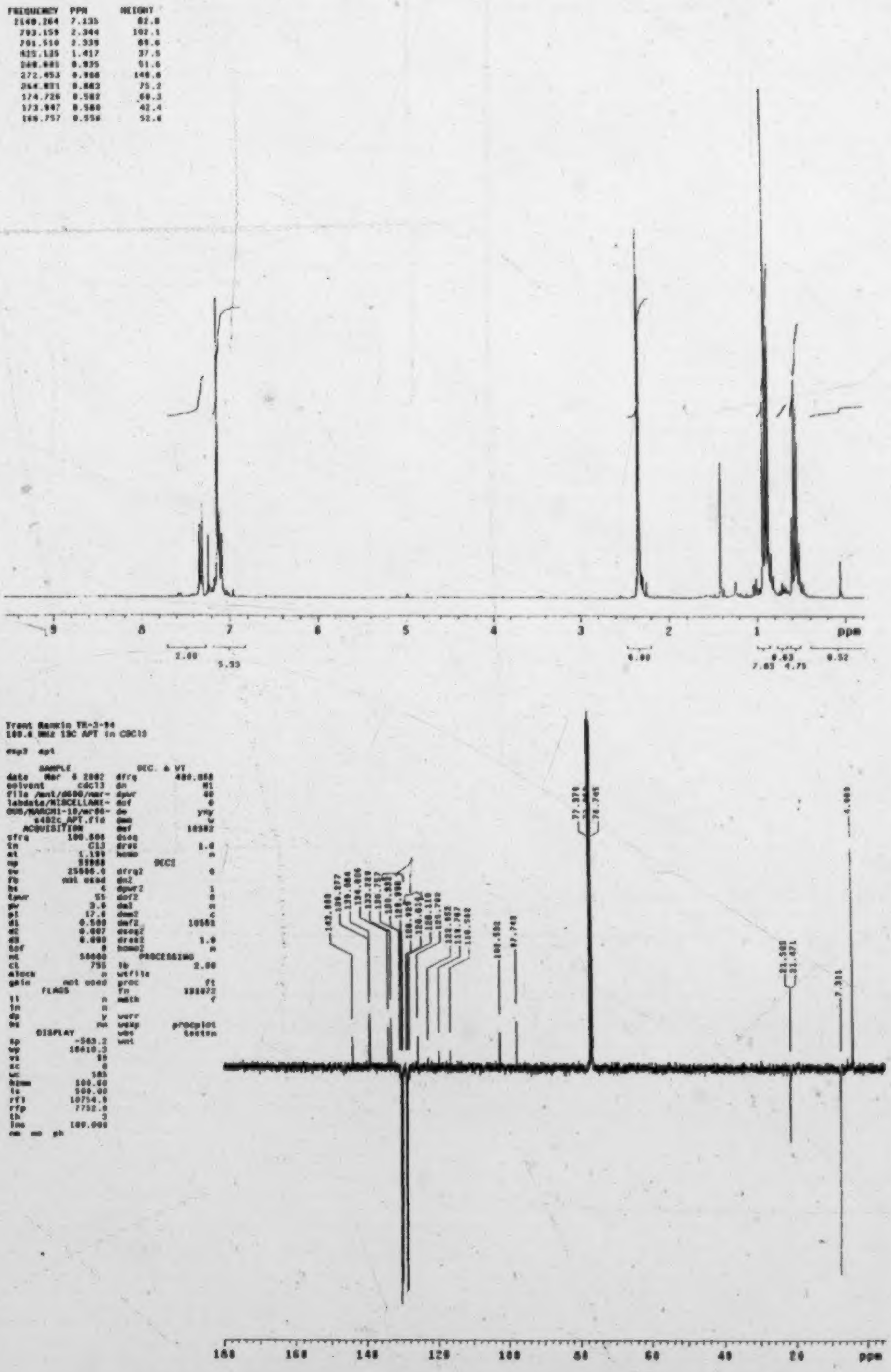
```
INDEX   FREQUENCY  PPM    WEIGHT
  1     2203.232   7.345    36.1
  2     2200.943   7.337    47.9
  3     2197.233   7.325    39.6
  4     2195.768   7.320    30.4
  5     2170.077   7.234    26.1
  6      280.768   0.936    52.0
  7      280.238   0.934    56.4
  8      272.636   0.909   160.0
  9      264.576   0.882    80.1
 10      182.419   0.608    27.0
 11      174.588   0.582    67.5
 12      166.803   0.556    60.5
```



```
Trent Rankin, TR-3-102
100 MHz APT in CDCl3 (ref. to CDCl3 @ 77
.0 ppm), temp 28.0 C -> actual temp = 28
.0 C, sw400 probe

CH, CH3 positive; C, CH2 negative


exp1  apt

      SAMPLE               DEC. & VT
date   Mar 19 2002  dn               H1
solvent      cdcl3  dof               0
file /mnt/d600/nmr- dm              yny
labdata/MISCELLANE- dmm               w
OUS/MARCH10-20/mrl- dmf            9524
   9s404c_apt.fid   dpwr             39
   ACQUISITION      temp           27.0
sfrq       100.603     PROCESSING
tn             C13  lb             2.00
at           2.400  wtfile
np          131072  proc             ft
sw         27210.9  fn         not used
fb        not used  math              f
bs               8
ss               8  werr
tpwr            55  wexp
pw             2.9  wbs
p1            17.6  wnt
d1           0.500        DISPLAY
d2           0.007  sp           -749.0
d3           0.001  wp          18100.2
tof         2049.3  vs             5407
nt           1e+06  sc                0
ct            1409  wc              160
alock            n  hzmm         100.60
gain            46  is           500.00
      FLAGS         rfl          9805.6
il               n  rfp          7751.6
in               n  th                3
dp               y  ins         100.000
hs              nn  ai    ph
```

143.840
138.485
138.065
130.394
130.055
129.271
128.155
126.351
126.070
120.349
119.019
118.028
103.056
97.418
77.378
77.060
76.742
30.380
7.811
3.934
160
140
120
100
80
60
40
20
ppm

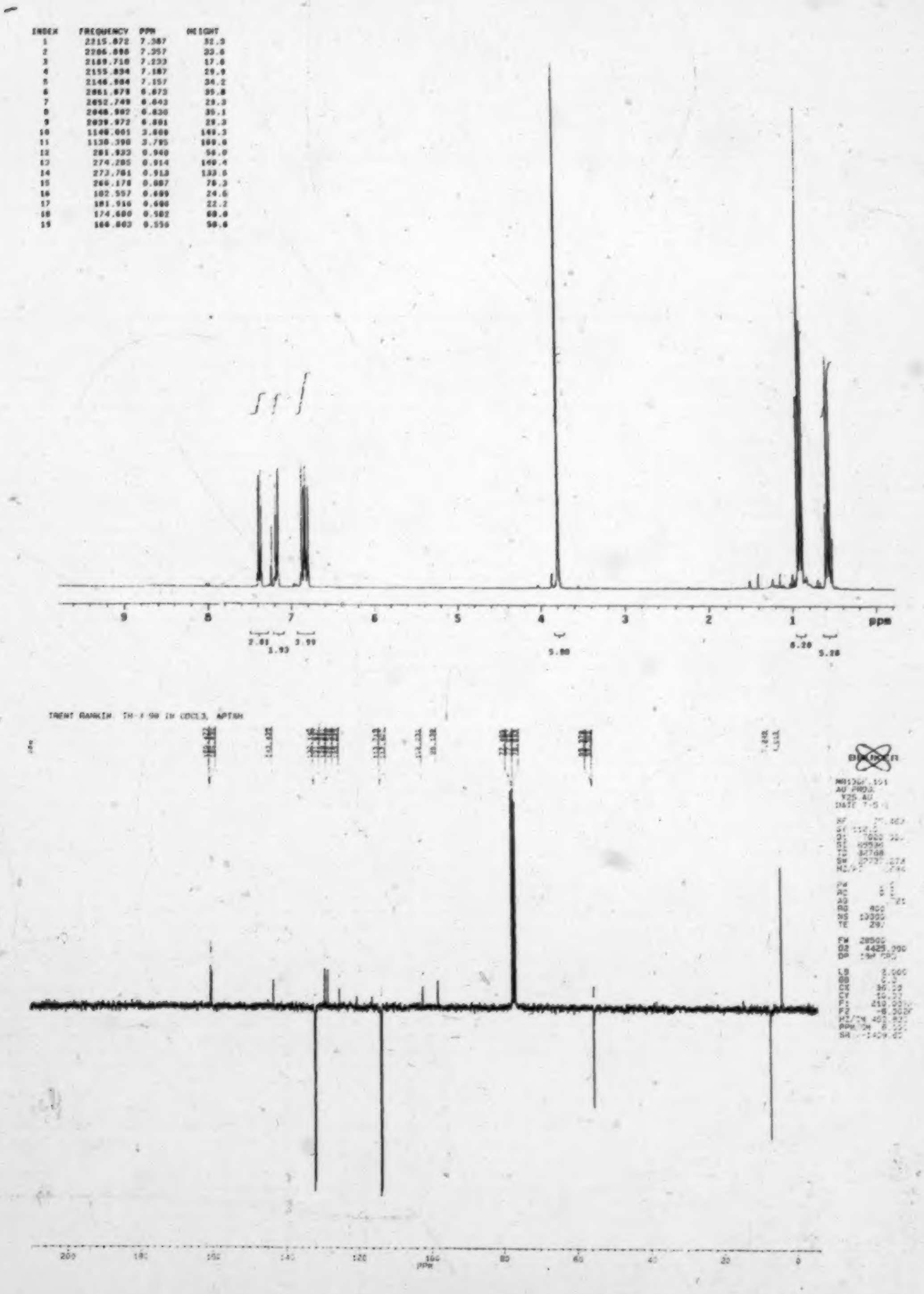
Figure 32 ^{1}H and ^{13}C NMR Spectra of Compound 23



```
FREQUENCY  PPM      HEIGHT
 2140.264  7.135      82.8
  703.159  2.344     102.1
  701.510  2.339      89.6
  425.135  1.417      37.5
[illegible]  0.835      51.6
  272.453  0.908     140.8
  264.931  0.883      75.2
  174.726  0.582      60.3
  173.947  0.580      42.4
  166.757  0.556      52.6
```

Trent Rankin TR-3-94
100.6 MHz 13C APT in CDCl3
exp3 apt

Figure 33. ^1H and ^{13}C NMR Spectra of Compound 24



INDEX	FREQUENCY	PPM	HEIGHT
1	2215.872	7.387	32.3
2	2206.896	7.357	33.6
3	2169.710	7.233	17.6
4	2155.834	7.187	29.9
5	2146.904	7.157	34.2
6	2061.879	6.873	35.8
7	2052.749	6.843	29.3
8	2048.902	6.830	35.1
9	2039.972	6.801	29.3
10	1140.001	3.800	149.3
11	1138.390	3.795	160.6
12	281.933	0.940	56.0
13	274.205	0.914	140.4
14	273.761	0.913	133.6
15	266.178	0.887	78.3
16	182.557	0.609	24.6
17	181.916	0.606	22.2
18	174.600	0.582	68.0
19	166.803	0.556	58.6

TRENT RANKIN TH-4-90 IN CDCL3, APTSH

9
8
7
6
5
4
3
2
1
ppm
2.01
3.93
3.99
5.90
6.20
5.28
BRUKER
200
180
160
140
120
100
PPM
80
60
40
20
0

Figure 34. ^1H and ^{13}C NMR Spectra of Compound 25

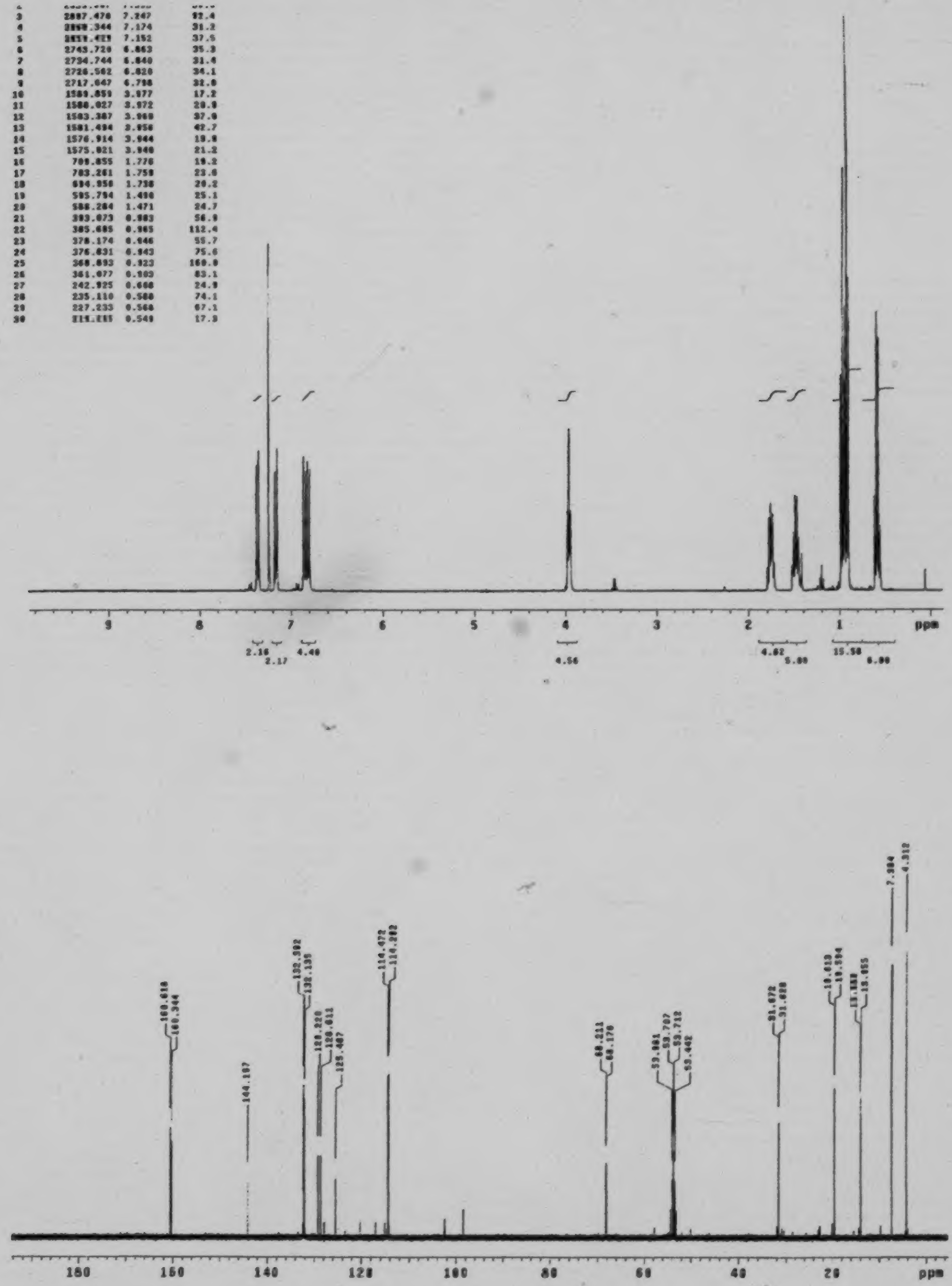


Figure 35. ¹H and ¹³C NMR Spectra of Compound 26

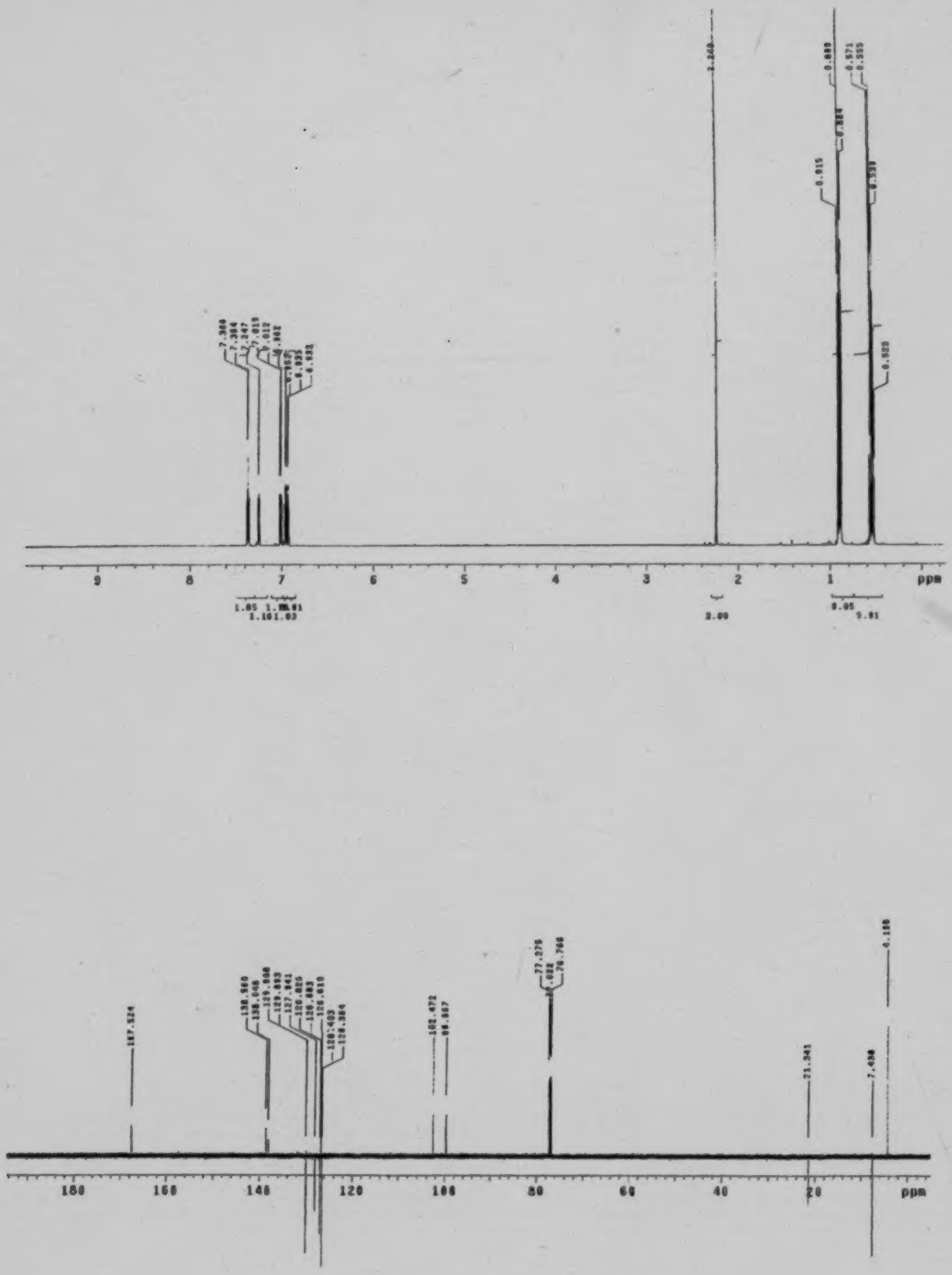


Figure 36. ^{1}H and ^{13}C NMR Spectra of Compound 27

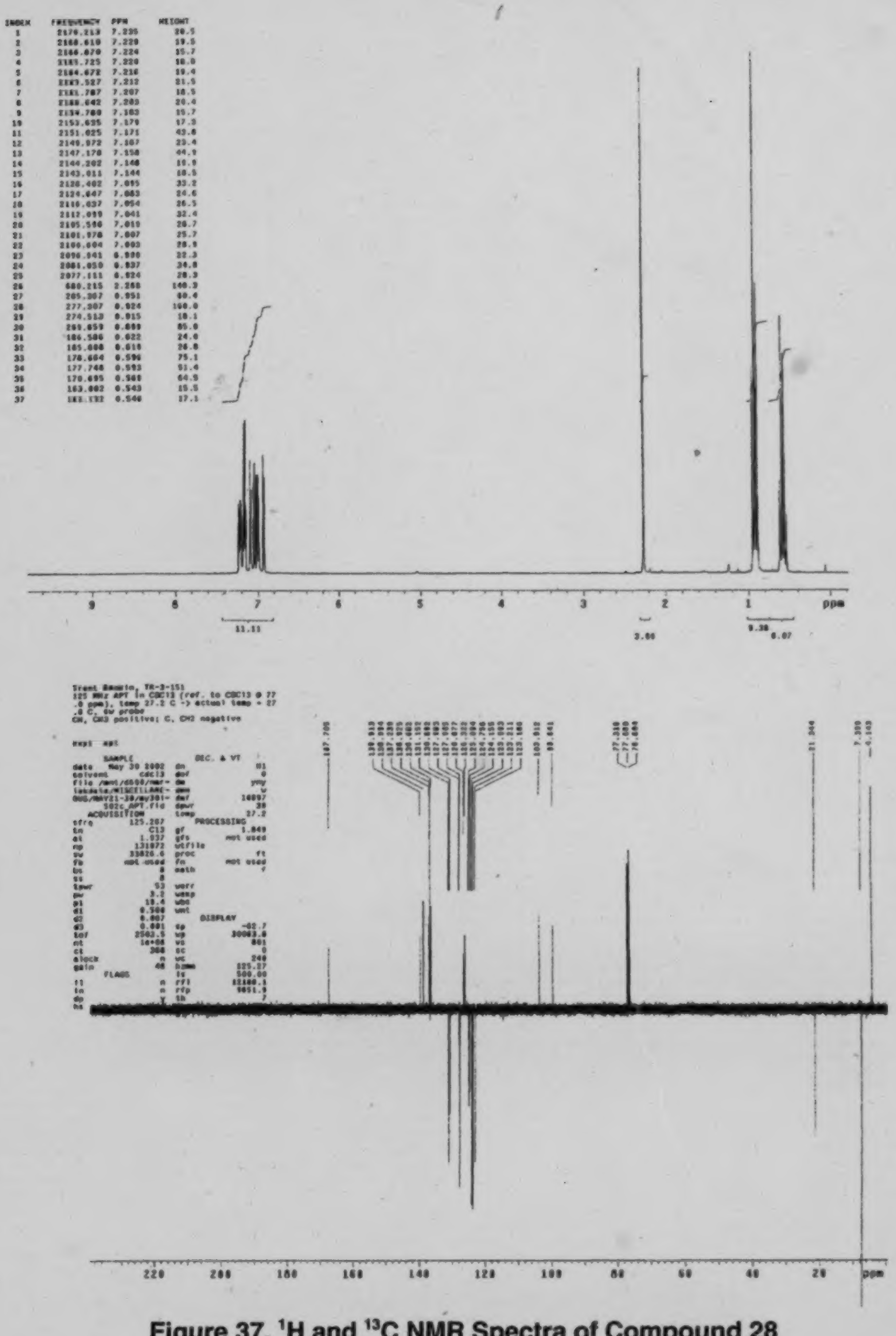
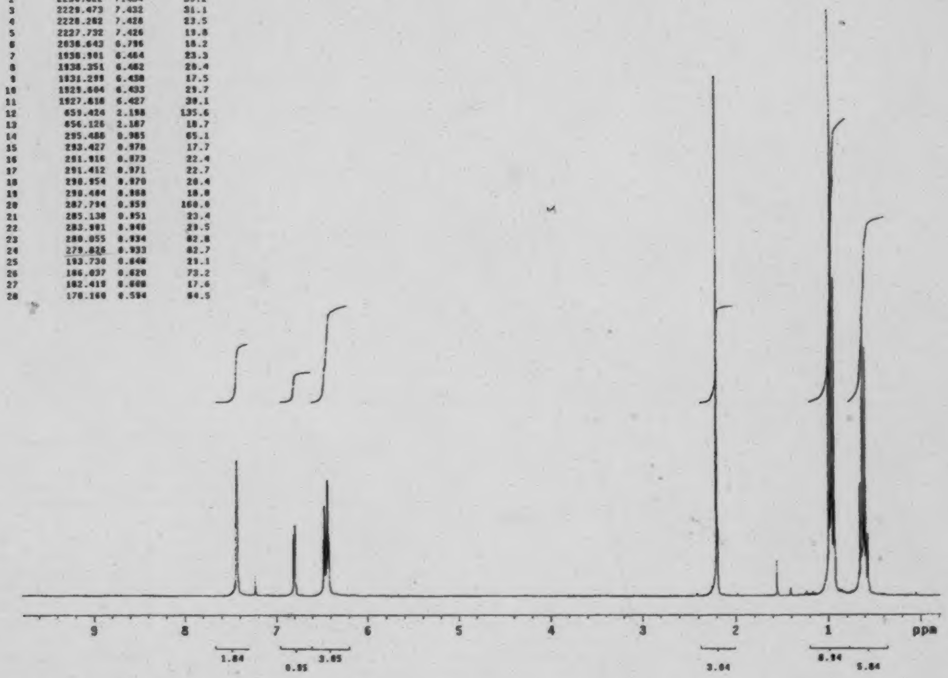


Figure 37. ^{1}H and ^{13}C NMR Spectra of Compound 28

INDEX	FREQUENCY	PPM	HEIGHT
1	2231.854	7.440	19.0
2	2230.022	7.434	35.2
3	2229.473	7.432	31.1
4	2228.282	7.428	23.5
5	2227.732	7.426	19.8
6	2038.643	6.796	18.2
7	1938.901	6.464	23.3
8	1938.351	6.462	20.4
9	1931.299	6.438	17.5
10	1929.604	6.433	29.7
11	1927.818	6.427	30.1
12	659.424	2.198	135.6
13	656.126	2.187	18.7
14	295.488	0.985	65.1
15	293.427	0.978	17.7
16	291.916	0.973	22.4
17	291.412	0.971	22.7
18	290.954	0.970	20.4
19	290.404	0.968	18.0
20	287.794	0.959	160.0
21	285.138	0.951	23.4
22	283.901	0.946	29.5
23	280.055	0.934	82.8
24	279.826	0.933	82.7
25	193.730	0.646	29.1
26	186.037	0.620	73.2
27	182.419	0.608	17.6
28	178.160	0.594	64.5



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labdata/MISCELLANE~  dof              0
OUS/JUNE21-30/jn26~  dm             yny
     s400c_APT.fid   dmm              w
   ACQUISITION       dmf          10582
sfrq       100.588   dseq
tn             C13   dres           1.0
at           1.104   homo             n
np           65536   temp          24.0
sw         28149.2          DEC2
fb        not used   dfrq2            0
bs               4   dn2
tpwr            55   dpwr2            1
pw             3.0   dof2             0
p1            17.6   dm2              n
d1           0.500   dmm2             c
d2           0.007   dmf2         10582
d3           0.001   dseq2
tof         1546.3   dres2          1.0
nt           50000   homo2            n
ct             314       PROCESSING
alock            n   lb            2.00
gain      not used   wtfile
      FLAGS          proc            ft
il               n   fn          262144
in               n   math             f
dp               y
hs              nn   werr
     DISPLAY         wexp      procplot
sp           -20.9   wbs         testsn
wp         18107.5   wnt
vs              33
sc               0
wc             180
hzmm        100.60
is          500.00
rfl        10781.3
rfp         7751.2
th               4
ins        100.000
nm  no  ph
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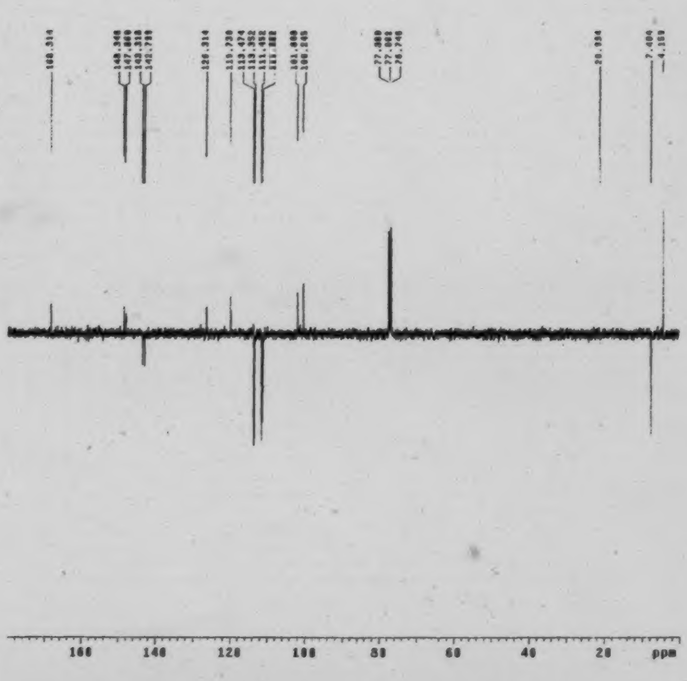
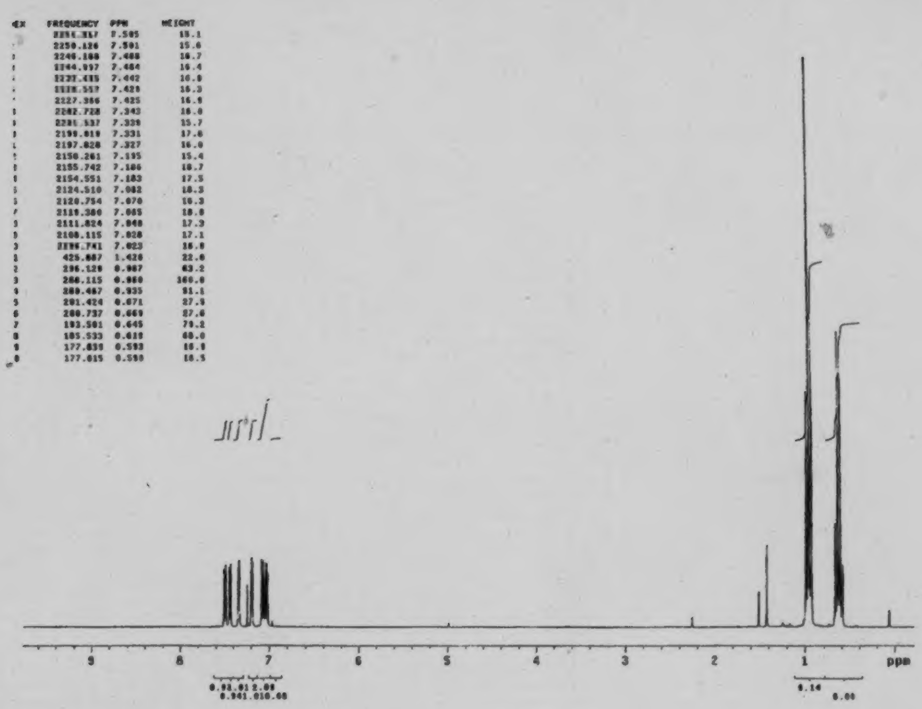


Figure 38. ^{1}H and ^{13}C NMR Spectra of Compound 29



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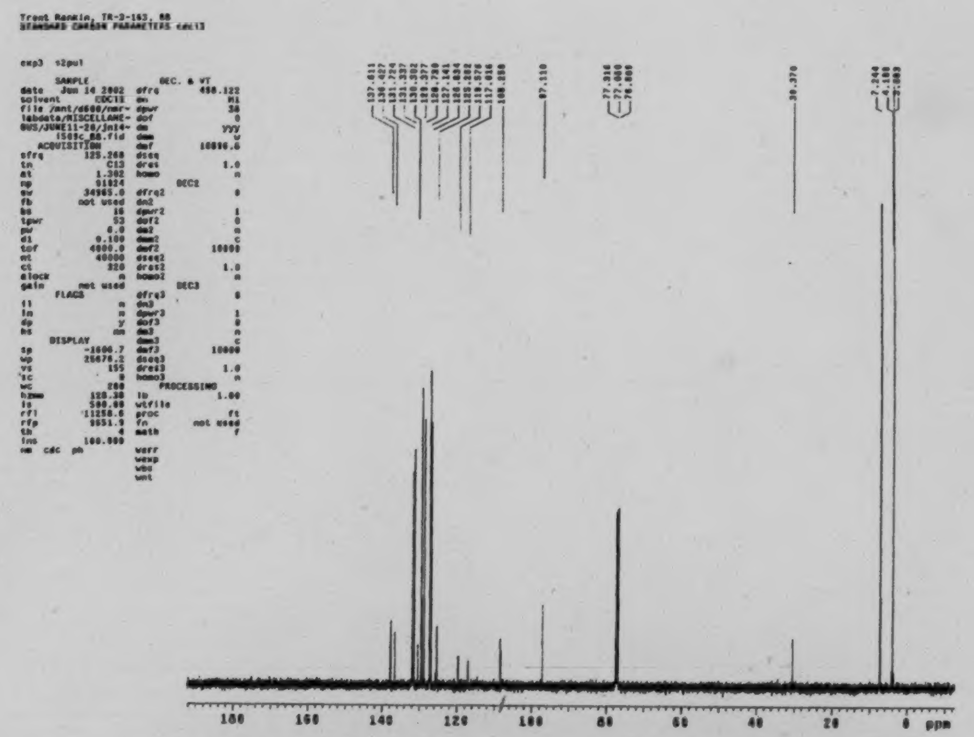
EX     FREQUENCY   PPM      HEIGHT
        2251.317  7.505      15.1
        2250.126  7.501      15.6
        2246.188  7.488      16.7
        2244.997  7.484      16.4
        2232.415  7.442      16.0
        2228.557  7.428      16.3
        2227.366  7.425      16.9
        2202.728  7.343      16.0
        2201.537  7.339      15.7
        2199.019  7.331      17.0
        2197.828  7.327      16.0
        2158.261  7.195      15.4
        2155.742  7.186      18.7
        2154.551  7.183      17.5
        2124.510  7.082      18.3
        2120.754  7.070      16.3
        2119.300  7.065      18.0
        2111.824  7.040      17.3
        2108.115  7.028      17.1
        2106.741  7.023      18.0
         425.887  1.420      22.0
         296.120  0.987      63.2
         288.115  0.960     100.0
         280.487  0.935      91.1
         201.424  0.671      27.9
         200.737  0.669      27.6
         193.501  0.645      71.2
         185.533  0.618      40.0
         177.839  0.593      18.0
         177.015  0.590      18.5
```



```
Trent Rankin, TR-2-163, 80
STANDARD CARBON PARAMETERS cdcl3

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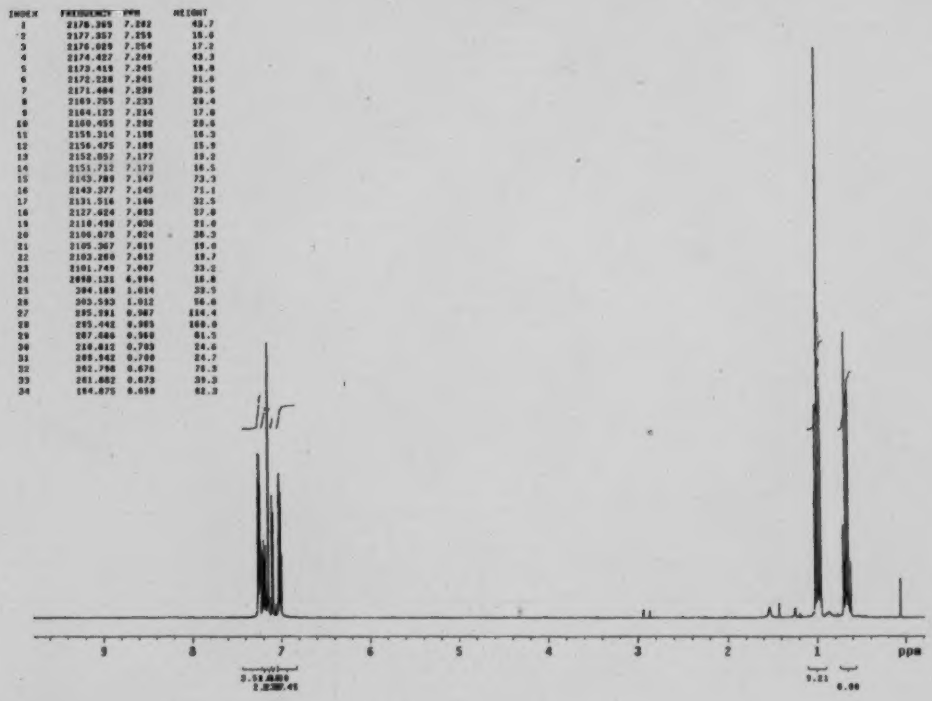
solvent      CDCl3   dn              H1
file /ant/d600/nmr-  dpwr            38
labdata/MISCELLANE-  dof              0
OUS/JUNE11-20/jn14-  dm             yyy
      1509c_80.fid   dmm              w
   ACQUISITION       dmf        10096.0
sfrq       125.268   dseq
tn             C13   dres           1.0
at           1.302   homo             n
np           91024         DEC2
sw         34965.0   dfrq2            0
fb        not used   dn2
bs              16   dpwr2            1
tpwr            53   dof2             0
pw             6.0   dm2              n
d1           0.100   dmm2             c
tof         4000.0   dmf2         10000
nt           40000   dseq2
ct             320   dres2          1.0
alock            n   homo2            n
gain      not used         DEC3
      FLAGS          dfrq3            0
il               n   dn3
in               n   dpwr3            1
dp               y   dof3             0
hs              nn   dm3              n
     DISPLAY         dmm3             c
sp         -1606.7   dmf3         10000
wp         25678.2   dseq3
vs             155   dres3          1.0
sc               0   homo3            n
wc             200       PROCESSING
hzmm        128.38   lb            1.00
is          500.00   wtfile
rfl        11258.6   proc            ft
rfp         9651.9   fn        not used
th               4   math             f
ins        100.000
nm  cdc  ph          werr
                     wexp
                     wbs
                     wnt
```

137.611
136.427
131.724
131.337
130.302
129.377
128.730
127.141
126.034
125.202
119.576
117.016
108.250
97.110
77.316
77.060
76.805
30.370
7.244
4.100
3.003
180
160
140
120
100
80
60
40
20
0
ppm

Figure 39. ^{1}H and ^{13}C NMR Spectra of Compound 30



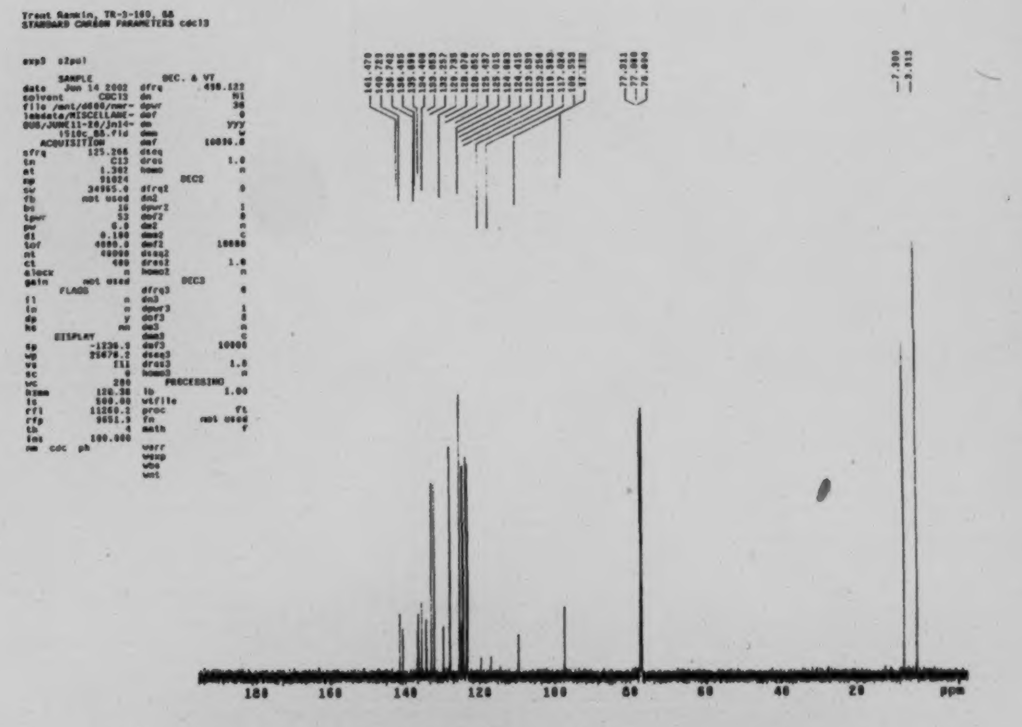


Figure 40. ^{1}H and ^{13}C NMR Spectra of Compound 31

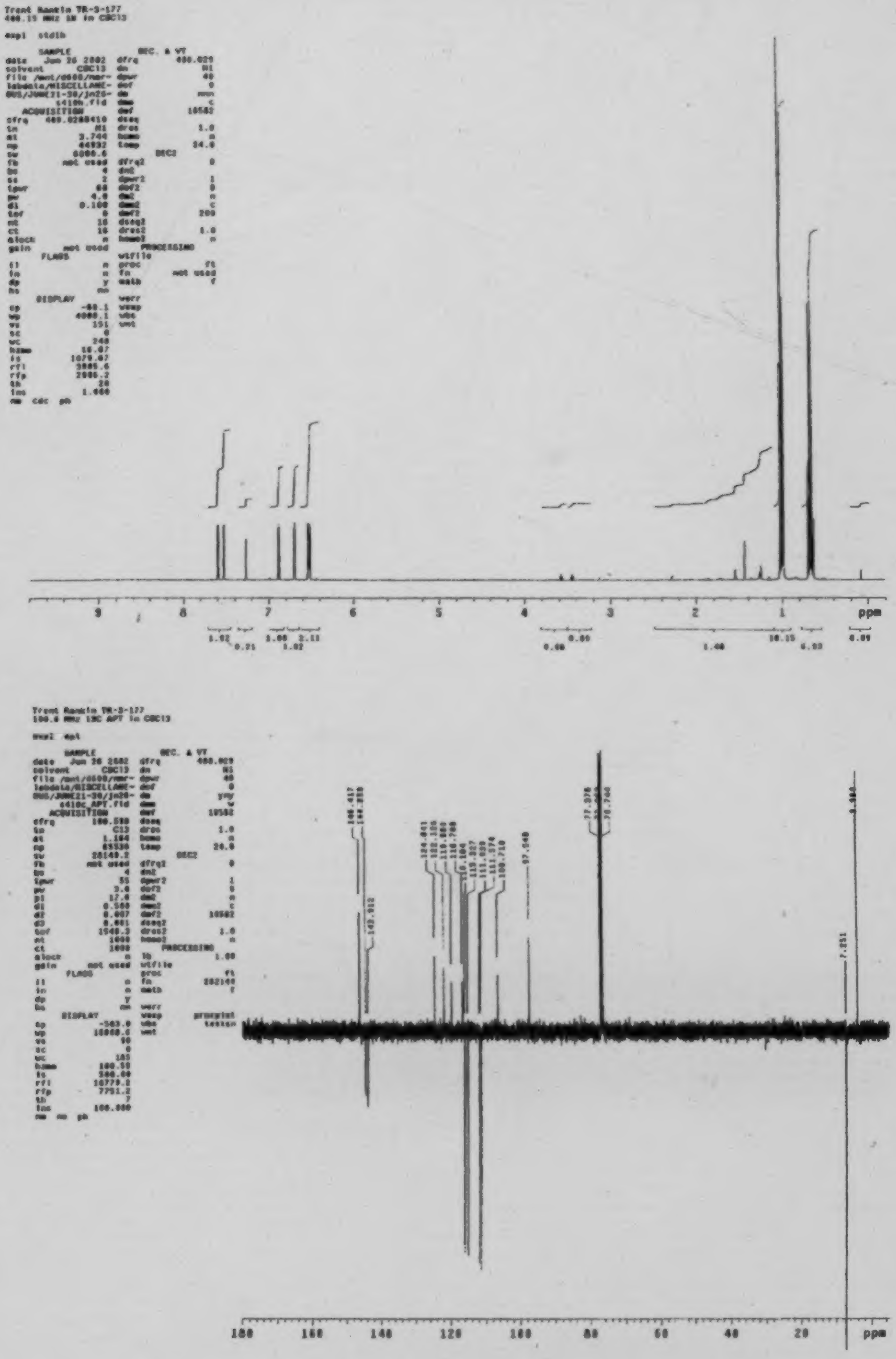


Figure 41. ^{1}H and ^{13}C NMR Spectra of Compound 32

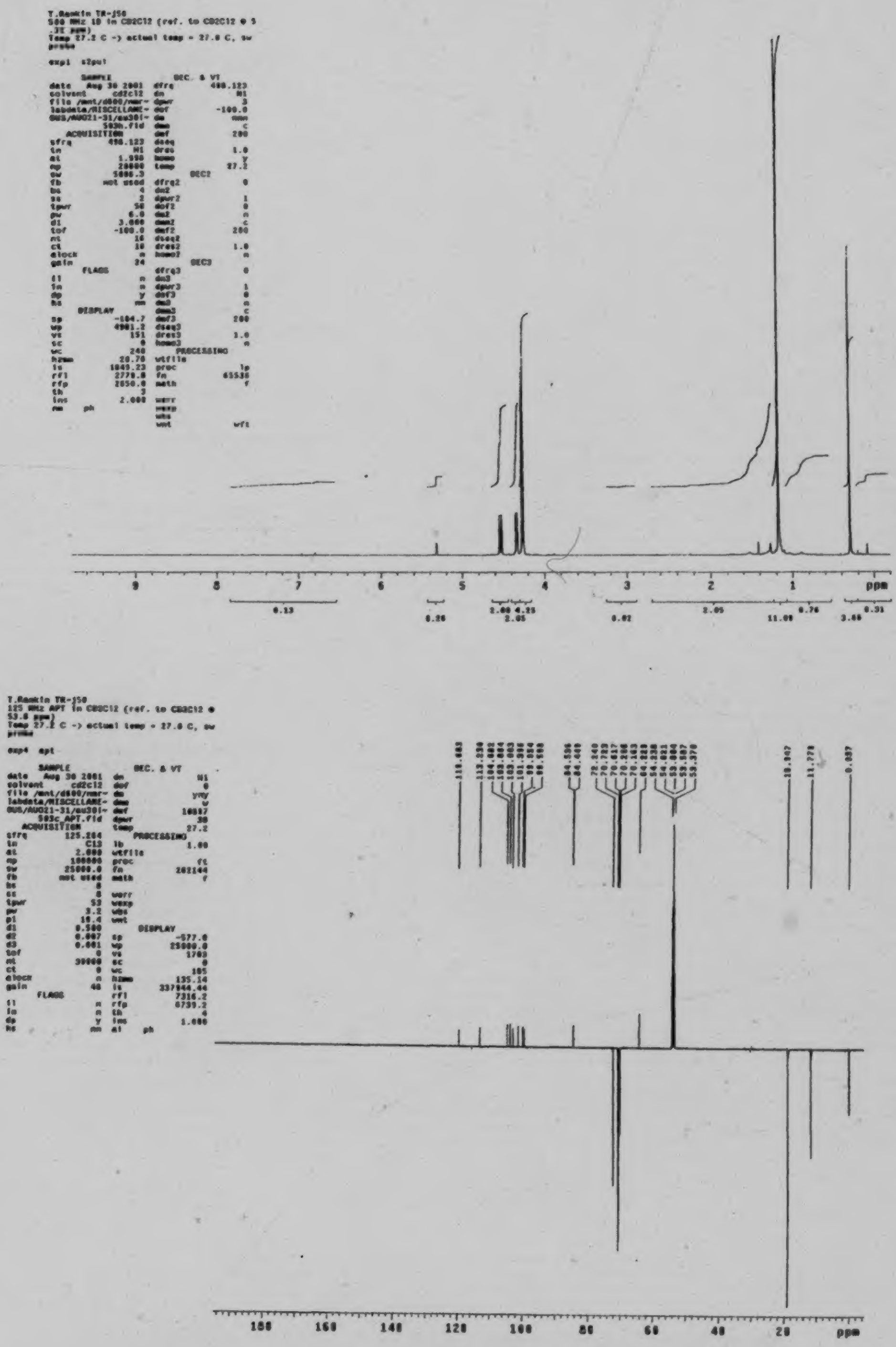
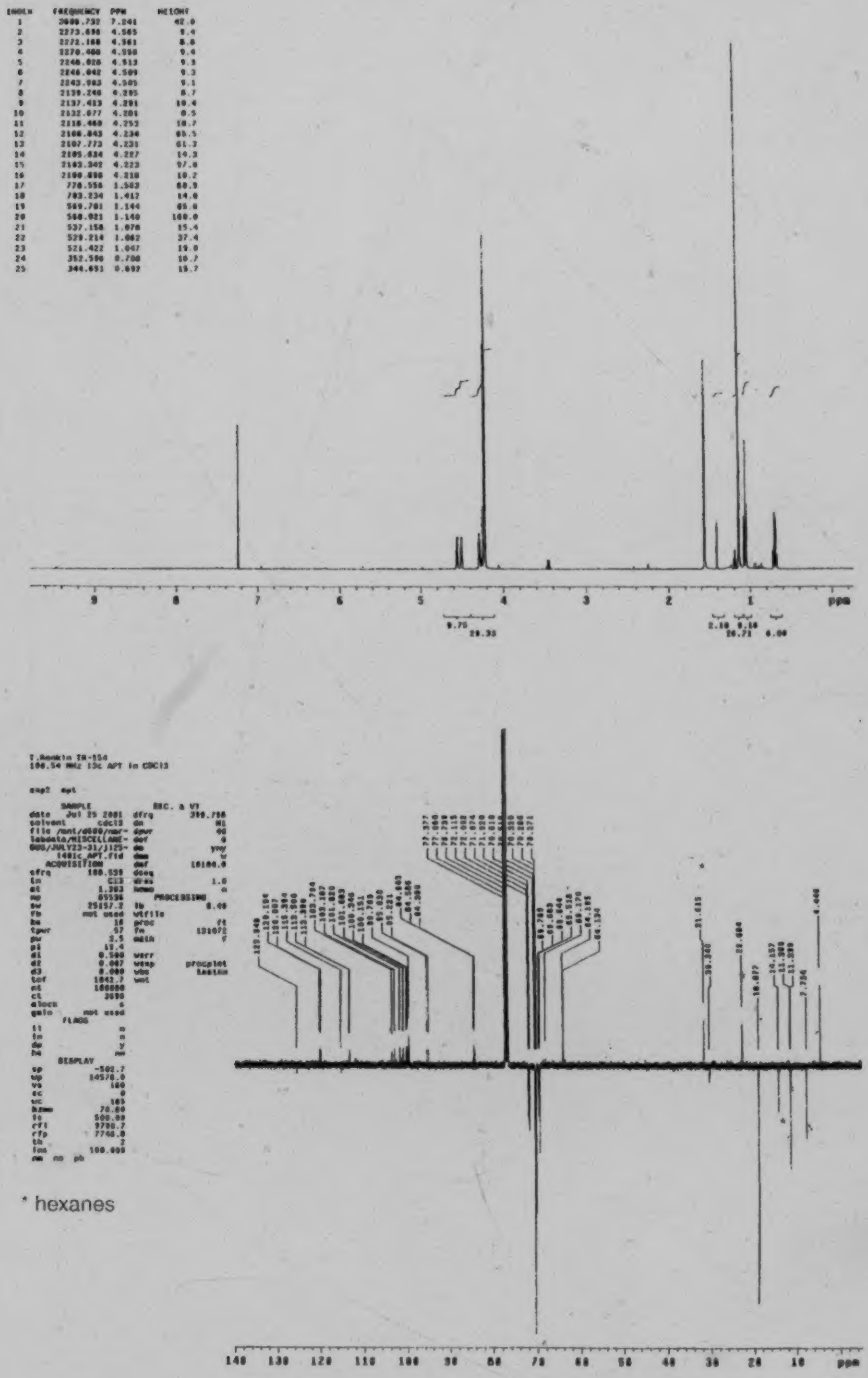


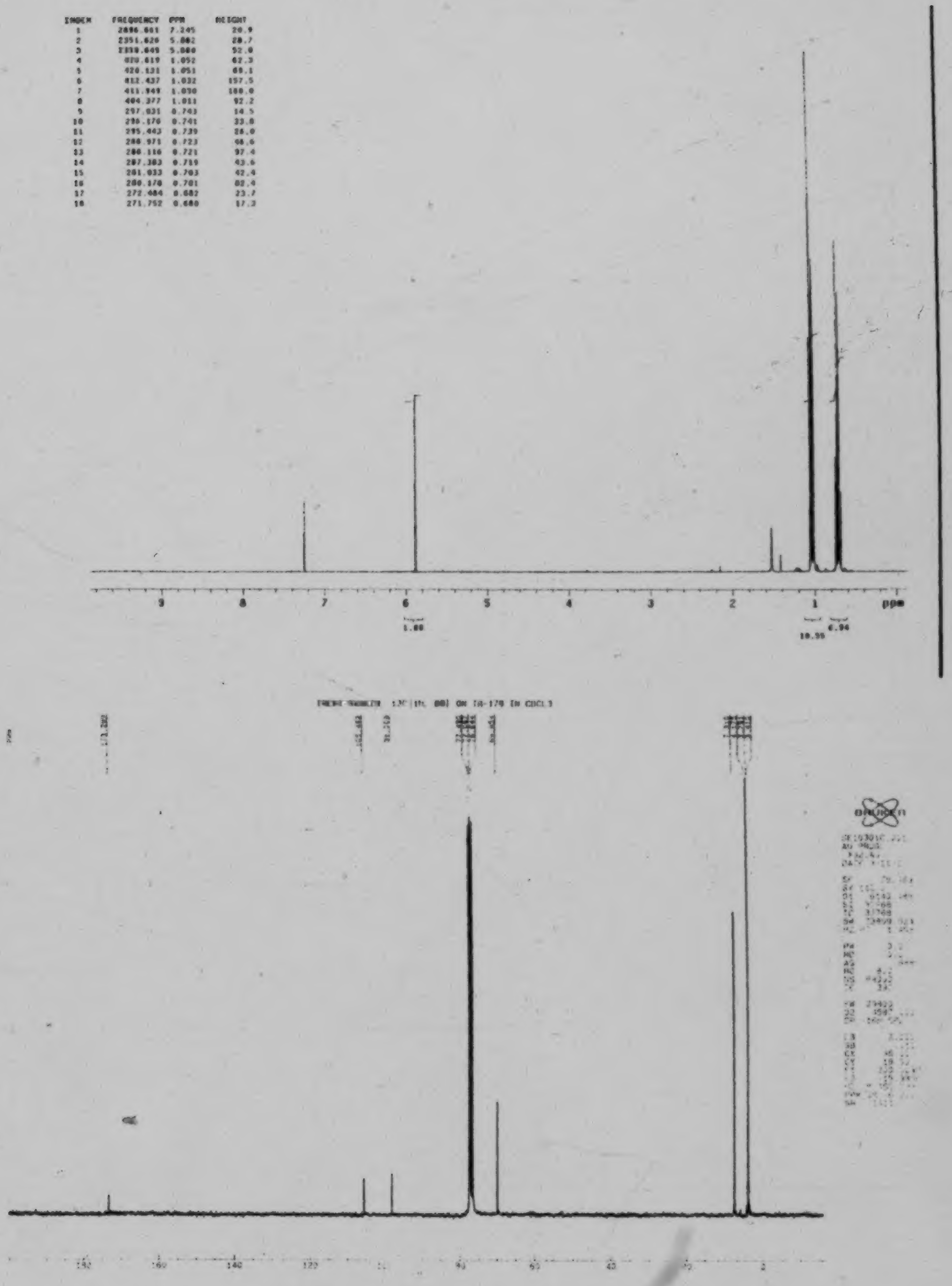
Figure 42. ^{1}H and ^{13}C NMR Spectra of Compound 42



INDEX	FREQUENCY	PPM	HEIGHT
1	3608.732	7.241	42.0
2	2273.698	4.565	9.4
3	2272.168	4.561	8.8
4	2270.480	4.558	9.4
5	2248.028	4.513	9.3
6	2246.042	4.509	9.3
7	2243.983	4.505	9.1
8	2139.246	4.295	8.7
9	2137.413	4.291	10.4
10	2132.077	4.281	8.5
11	2118.460	4.253	10.7
12	2108.843	4.234	65.5
13	2107.773	4.231	61.3
14	2105.834	4.227	14.3
15	2103.342	4.223	97.0
16	2100.898	4.218	10.2
17	778.556	1.563	60.9
18	703.234	1.412	14.6
19	569.701	1.144	65.6
20	568.021	1.140	100.0
21	537.158	1.078	15.4
22	529.214	1.062	37.4
23	521.422	1.047	19.8
24	352.596	0.708	16.7
25	346.651	0.697	15.7

* hexanes

Figure 43. ^{1}H and ^{13}C NMR Spectra of Compound 43



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INDEX   FREQUENCY   PPM     HEIGHT
  1      2896.661  7.245      20.9
  2      2351.626  5.882      28.7
  3      2350.849  5.880      52.0
  4       420.619  1.052      62.3
  5       420.131  1.051      69.1
  6       412.437  1.032     157.5
  7       411.949  1.030     100.0
  8       404.377  1.011      92.2
  9       297.031  0.743      14.5
 10       296.176  0.741      33.0
 11       295.443  0.739      26.0
 12       288.971  0.723      46.6
 13       288.116  0.721      97.4
 14       287.383  0.719      43.6
 15       281.033  0.703      42.4
 16       280.178  0.701      82.4
 17       272.484  0.682      23.7
 18       271.752  0.680      17.3
```
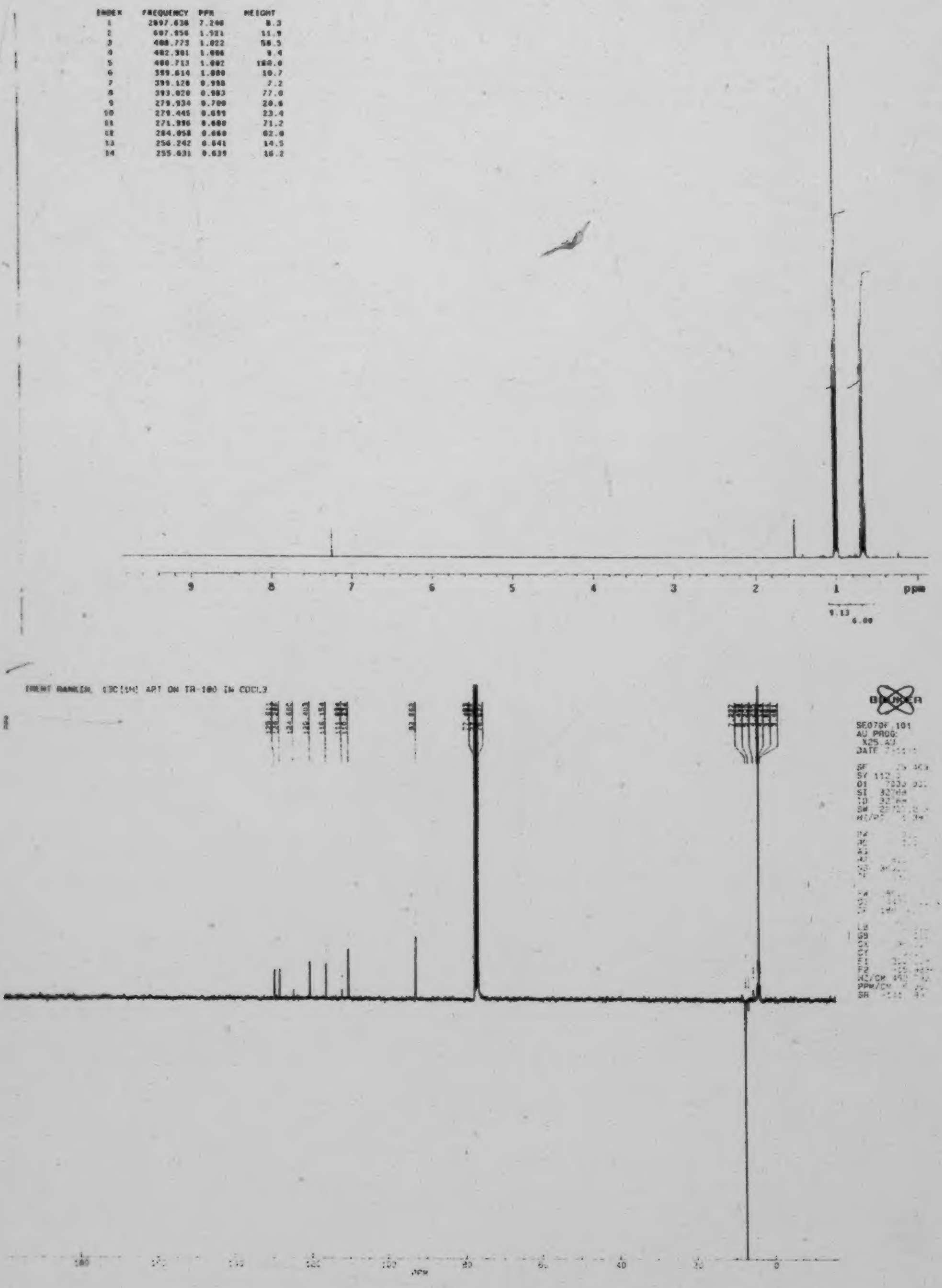
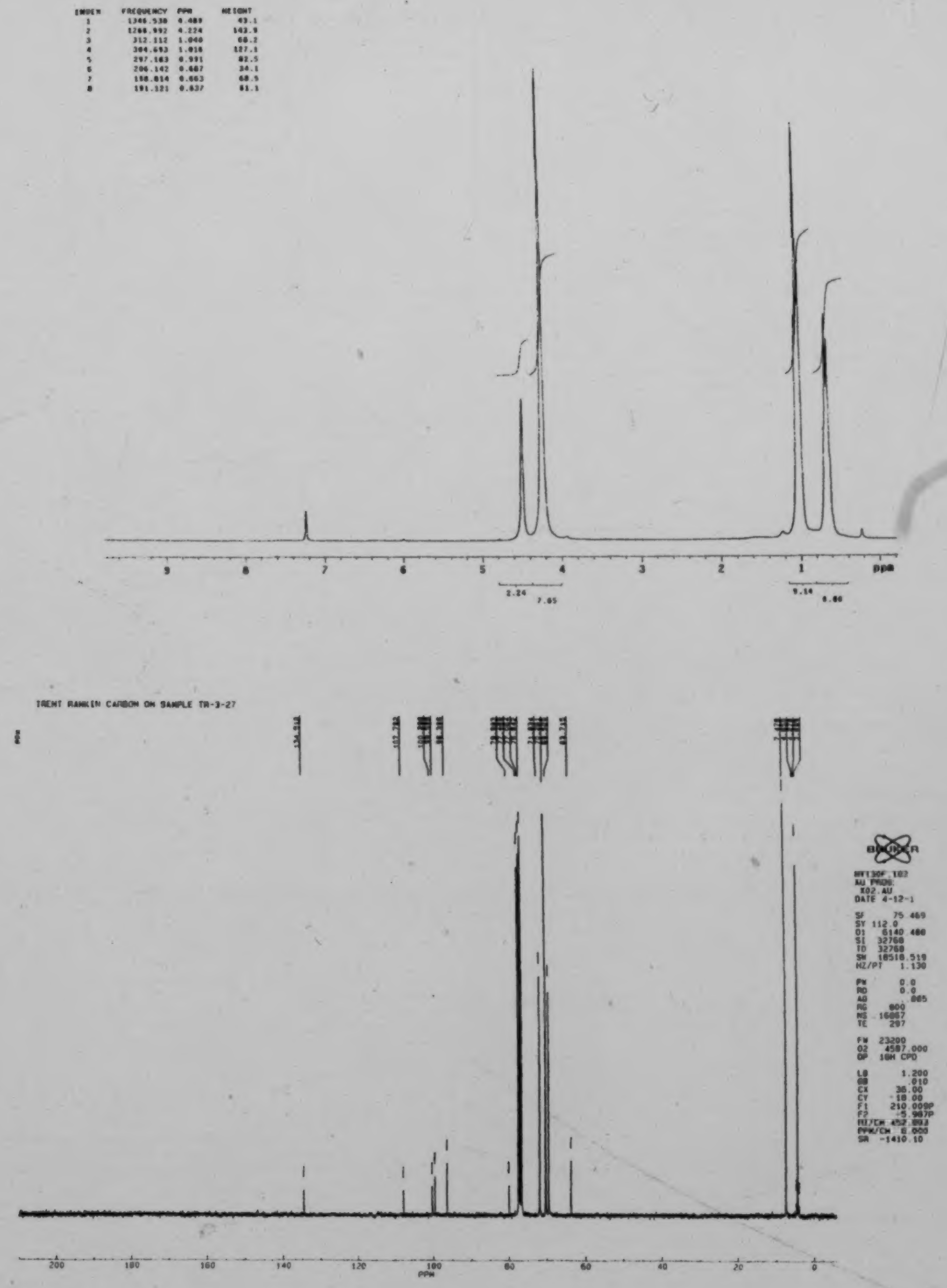

Figure 44. ^{1}H and ^{13}C NMR Spectra of Compound 44



INDEX	FREQUENCY	PPM	HEIGHT
1	2897.638	7.240	8.3
2	607.956	1.521	11.9
3	408.773	1.022	58.5
4	402.381	1.006	9.4
5	400.713	1.002	100.0
6	399.614	1.000	10.7
7	399.120	0.998	7.2
8	393.020	0.983	77.0
9	279.934	0.700	20.6
10	279.445	0.699	23.4
11	271.996	0.680	71.2
12	264.058	0.660	62.0
13	256.242	0.641	14.5
14	255.631	0.639	16.2

Figure 45. ^{1}H and ^{13}C NMR Spectra of Compound 45



INDEX	FREQUENCY	PPM	HEIGHT
1	1346.538	4.489	43.1
2	1268.992	4.224	143.9
3	312.112	1.040	68.2
4	304.693	1.016	127.1
5	297.183	0.991	82.5
6	206.142	0.687	34.1
7	198.814	0.663	68.5
8	191.121	0.637	61.1

Figure 46. ^{1}H and ^{13}C NMR Spectra of Compound 46

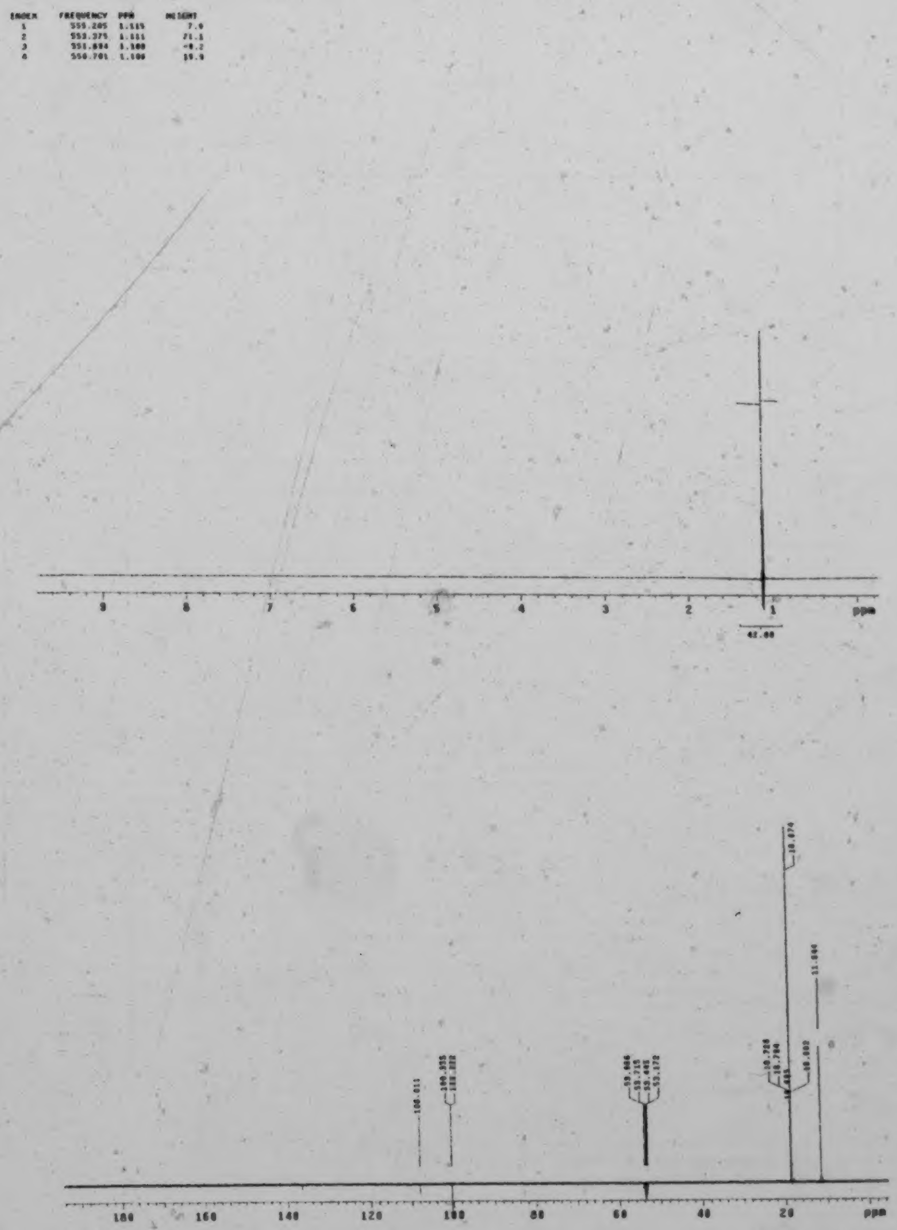


Figure 47. ¹H and ¹³C NMR Spectra of Compound 48